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Occurrence and geochemistry of radium in water from principal drinking-water aquifer systems of the United States

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abstract

A total of 1270 raw-water samples (before treatment) were collected from 15 principal and other major aquifer systems (PAs) used for drinking water in 45 states in all major physiographic provinces of the USA and analyzed for concentrations of the Ra isotopes ^{224}Ra, ^{226}Ra and ^{228}Ra establishing the framework for evaluating Ra occurrence. The US Environmental Protection Agency Maximum Contaminant Level (MCL) of 0.185 Bq/L (5 pCi/L) for combined Ra (^{226}Ra plus ^{228}Ra) for drinking water was exceeded in 4.02% (39 of 971) of samples for which both ^{226}Ra and ^{228}Ra were determined, or in 3.15% (40 of 1266) of the samples in which at least one isotope concentration (^{226}Ra or ^{228}Ra) was determined. The maximum concentration of combined Ra was 0.755 Bq/L (20.4 pCi/L) in water from the North Atlantic Coastal Plain quartzose sand aquifer system. All the exceedences of the MCL for combined Ra occurred in water samples from the following 7 PAs (in order of decreasing relative frequency of occurrence): the Midcontinent and Ozark Plateau Cambro-Ordovician dolomites and sandstones, the North Atlantic Coastal Plain, the Floridan, the crystalline rocks (granitic, metamorphic) of New England, the Mesozoic basins of the Appalachian Piedmont, the Gulf Coastal Plain, and the glacial sands and gravels (highest concentrations in New England).

The concentration of Ra was consistently controlled by geochemical properties of the aquifer systems, with the highest concentrations most likely to be present where, as a consequence of the geochemical environment, adsorption of the Ra was slightly decreased. The result is a slight relative increase in Ra mobility, especially notable in aquifers with poor sorptive capacity (Fe-oxide-poor quartzose sands and carbonates), even if Ra is not abundant in the aquifer solids. The most common occurrence of elevated Ra throughout the USA occurred in anoxic water (low dissolved-O_2) with high concentrations of Fe or Mn, and in places, high concentrations of the competing ions Ca, Mg, Ba and Sr, and occasionally of dissolved solids, K, SO_4 and HCO_3. The other water type to frequently contain elevated concentrations of the Ra radioisotopes was acidic (low pH), and had in places, high concentrations of NO_3 and other acid anions, and on occasion, of the competing divalent cations, Mn and Al. One or the other of these broad water types was commonly present in each of the PAs in which elevated concentrations of combined Ra occurred. Concentrations of ^{226}Ra or ^{228}Ra or combined Ra correlated significantly with those of the above listed water-quality constituents (on the basis of the non-parametric Spearman correlation technique) and loaded on principal components describing the above water types from the entire data set and for samples from the PAs with the highest combined Ra concentrations.

Concentrations of ^{224}Ra and ^{226}Ra were significantly correlated to those of ^{228}Ra (Spearman's rank correlation coefficient, +0.236 and +0.326, respectively). Activity ratios of $^{224}Ra/^{228}Ra$ in the water samples were mostly near 1 when concentrations of both isotopes were greater than or equal to 0.037 Bq/L (1 pCi/L), the level above which analytical results were most reliable. Co-occurrence among these highest concentrations of the Ra radionuclides was most likely in those PAs where chemical conditions are most conducive to Ra mobility (e.g. acidic North Atlantic Coastal Plain). The concentrations of ^{224}Ra were occasionally greater than 0.037 Bq/L and the ratios of $^{224}Ra/^{228}Ra$ were generally highest in the PAs composed of alluvial sands and Cretaceous/Tertiary sandstones from the western USA, likely because concentrations of ^{224}Ra are enhanced in solution relative to those of ^{228}Ra by alpha recoil from the aquifer matrix. Rapid adsorption of the two Ra isotopes (controlled by the alkaline and oxic aquifer

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geochemistry) combined with preferential faster recoil of ^{224}Ra generates a $^{224}Ra/^{228}Ra$ ratio much greater than 1. The $^{228}Ra/^{226}Ra$ activity ratio was locally variable, and was generally lower than 1 (^{226}Ra rich) in samples from PAs with carbonate bedrock, but was typically greater than 1 (^{228}Ra rich) in PAs composed of unconsolidated sand.

1. Introduction

The US Geological Survey (USGS), as part of its National Water Quality Assessment (NAWQA) Program, and in cooperation with the US Environmental Protection Agency (USEPA), has been assessing the occurrence of selected naturally occurring radionuclides in ground water from principal and other major aquifer systems (PAs) used as sources of drinking water in the USA. This article summarizes the results of the nationwide sampling effort conducted to determine the occurrence of the 3 commonly occurring isotopes of Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra in water from the 15 PAs studied. In addition to concentrations of Ra isotopes, concentrations of U and ^{222}Rn, gross alpha- and beta-particle activities, and ancillary water-quality, geochemical, geologic, hydrologic, well-construction, land-use, and other related information were collected at well sites within the PAs. This information creates the framework for understanding Ra occurrence in drinking water from PAs in the USA, defines occurrence where data has been previously lacking on this scale including the west-central and western USA, and addresses issues regarding relationships of Ra occurrence with geology, geochemistry, and general measures of radioactivity, such as gross alpha-particle activity or concentrations of ^{222}Rn.

For more than 75 a, ingestion of Ra has been linked to human cancer risk (Evans, 1933), and cancer-risk estimates have changed little in that time (USEPA, 1999). The greatest health risk is due to Ra being sequestered efficiently into bone tissue, especially from water where Ra is present as the dissolved cation (Mays et al., 1985). The risk is presumed linearly proportional to exposure (amount and duration; USEPA, 1999). Provisional drinking-water standards for Ra (USEPA, 1976) became final with the Radionuclide Rule of 2000 (USEPA, 2000a). For Ra, the Maximum Contaminant Level (MCL) is established such that the sum of ^{226}Ra and ^{228}Ra (termed "combined Ra") cannot exceed 0.185 Bq/L (5 pCi/L; where 1 pCi/L equals 0.037 Bq/L). The other MCLs promulgated for radionuclides in 2000 are: gross alpha-particle activity (including ^{226}Ra but excluding U and ^{222}Rn), 0.555 Bq/L (15 pCi/L), gross beta-particle activity, 4 millirems per year (isotope specific dose), and U, 30 lg/L. Gross alpha-particle activity has also been suggested for use as a compliance-monitoring "screen" for combined Ra (Hess et al., 1985).

Knowledge of local and regional geochemical and hydrological conditions and the distributions of ^{226}Ra, ^{228}Ra, and ^{224}Ra radioisotopes, as well as those of U, can help water-resource managers and regulators prioritize scarce resources to use for monitoring, to assess exposure, and to inform and educate the local population, especially those consuming water from private drinking-water wells, about the regions most at risk of having high Ra concentrations. To insure water suppliers can meet the MCLs for combined Ra and that for gross alpha-particle activity requires knowledge of the local and regional distribution of both the ^{226}Ra and ^{228}Ra radioisotopes for the former MCL, as well as those of ^{224}Ra and U in addition to that of ^{226}Ra for the latter. If the MCLs cannot be met, knowledge of the local and regional geochemical and hydrological conditions and concentration distributions are of use in the search for an alternate supply. Data of various types and quality, including concentrations of one or more isotopes of Ra, primarily of ^{226}Ra and to a lesser extent, ^{228}Ra, have been collected and summarized in previous national Ra- or radionuclide-occurrence surveys (Scott and Barker, 1962; Hess et al., 1985; Longtin, 1988; Focazio et al., 2001). None of these surveys coupled data on Ra or radionuclide occurrence with extensive geologic, geochemical, and hydrologic information to provide characterization of the environments of Ra occurrence in the principal drinking-water aquifer systems of the USA.

The recent documentation by Parsa (1998), Focazio et al. (2001) and Szabo et al. (2005) showed that ^{224}Ra as well as ^{228}Ra are more widespread in major aquifers used for drinking water than originally estimated by Hess et al. (1985). Turner et al. (1961) first recognized the effect that the presence of ^{224}Ra in ground water may have on the measurement of gross alpha-particle activity. If the measurement takes place shortly (48–72 h) after sample collection, the ^{224}Ra and its progeny can contribute substantially to alpha-particle activity with the emission of about 0.10 Bq/L (2.7 pCi/L) of alpha particles for each 0.037 Bq/L (1 pCi/L) of ^{224}Ra present (Parsa, 1998; Szabo et al., 2005; Arndt and West, 2008; Arndt, 2010). Thus, 72 h after sample collection, a concentration of 0.20 Bq/L (5.5 pCi/L) of ^{224}Ra in a sample can result in a measured gross alpha-particle activity just about equal to (within 1%) the MCL (Parsa, 1998; Szabo et al., 2005). Consumers ingest the water mostly in this time frame, soon after it is pumped, within 3 days to one week. Conventional gross alpha-particle activity measurements are permissible 30 to even 90 days after sample collection, however. The monitoring and implementation guidance (USEPA, 2000b) recommends but does not mandate that gross alpha-particle activity be determined within 48–72 h in areas rich in Ra in order to account for the presence of the short-lived alpha-particle-emitting isotopes such as ^{224}Ra. The areas most needing these analyses require further definition and prioritization.

The results of the current study, based on water-concentration data from 1270 wells in 45 states, provides extensive geographical coverage of the USA, describes occurrence of and relationships among Ra isotopes, describes Ra isotope ratios where quantifiable, and describes the occurrence of the Ra isotopes in terms of specific geological and geochemical environments. The information on the geology, geochemistry, and hydrology associated with Ra occurrence was used to assess interplay among the important geochemical processes that control Ra mobility and the confluences with general geologic features of the PAs with the highest frequency of Ra occurrence. The results are also used to fill the data gaps described above by adding to the documentation of the distribution of isotopes of Ra in ground water used for drinking water, especially the occurrence of ^{224}Ra in the western USA where data was most lacking, and by examining contributions of isotopes of Ra, including ^{224}Ra, to gross alpha-particle activity there.

1.1. Naturally occurring radium

Radium in nature exists as one of four isotopes: ^{223}Ra, ^{224}Ra, ^{226}Ra or ^{228}Ra. The naturally occurring Ra radionuclides are derived from isotopes of U and Th, specifically long-lived ^{238}U, ^{235}U and ^{232}Th, which produce the various progeny isotopes, including those of Ra, and terminate with formation of stable isotopes of Pb. The ^{223}Ra isotope is a member of the ^{235}U decay series and, therefore, occurs less frequently in the environment in high concentrations than the other Ra isotopes because ^{235}U itself comprises about 0.72% of natural U. Given its limited occurrence, ^{223}Ra is not discussed further. The ^{226}Ra isotope is the sixth member of the ^{238}U decay series, has a half-life of about 1.622 ka, decays by alpha-particle emission and because of its long half-life, is the most abundant Ra isotope in the environment in terms of actual mass. The ^{228}Ra isotope is the second member of the ^{232}Th decay series, has a half-life of 5.75 a, and decays by beta-particle emission. The ^{224}Ra isotope is the fifth member of the ^{232}Th decay series, has a half-life of 3.64 days, and decays by alpha-particle emission. The relatively short half-life of ^{228}Ra and ^{224}Ra may limit the potential for unsupported transport (transport without the presence of an equivalent amount of the parent in solution) relative to that of the much longer-lived ^{226}Ra isotope, and thereby may lead to change in isotopic ratios in advecting ground water that has long residence time, especially in strata variably enriched in U and Th, and in sorptive clays and oxyhydroxides.

The occurrence of radionuclides in ground water depends first on the concentration and distribution of the parent element in the rock matrix, second on the solubility of the parent element, third on the solubility of the radionuclide itself, fourth on the rate of release of the radionuclide by weathering (leaching) and by recoil relative to the rate of geochemical reactions controlling or limiting mobility, and fifth on the residence time of the water. The occurrence of a parent radionuclide in solution does not necessarily indicate the presence of its decay products because of differences in chemical behavior. Chemically, Ra reacts similarly to other divalent alkaline-earth cations such as Ca and Sr, and is most similar to Ba (Langmuir and Riese, 1985; Gilkeson and Cowart, 1987). Both Ra and Ba are exclusively divalent cations in water, and do not undergo redox transformations; at high pH (near 10), they can form neutral or anionic (primarily SO_4) complexes (Langmuir and Riese, 1985). Radium can readily co-precipitate with Ba sulfate (barite), with Ba carbonate (witherite), or with Sr sulfate (celestite) when the constituents forming these salts are abundant enough in solution that they exceed solubility limits (Langmuir and Melchoir, 1985; Martin and Akber, 1999). Radium is not sufficiently abundant in nature to precipitate Ra sulfate salts, even though Ra sulfate is insoluble (Langmuir and Melchoir, 1985; Grundl and Cape, 2006). In dilute waters, Ra is chemically reactive (sorptive). Laboratory studies have shown that Ra is readily adsorbed by clay minerals (Ames et al., 1983a), but has an even stronger pattern of preferential adsorption to amorphous Fe- and Mn-oxyhydroxides (Moore and Reid, 1973; Ames et al., 1983b; Benes et al., 1984) to which it adsorbs in a matter of seconds to minutes (Krishnaswami et al., 1982). Analyses of natural Fe hydroxide samples have shown that they contain much more ^{226}Ra than surrounding rock matrix (Korner and Rose, 1977) and dissolution of the Fe- and Mn-oxyhydroxides releases Ra to the water (Landa et al., 1991). The increase in Ra mobility with an increase in mineralization is mostly attributed to the competitive exchange with similar ions, the so-called "competing ion" effect (Nathwani and Phillips, 1979) that has been documented for waters that are "mineralized" or saline (Kraemer and Reid, 1984; Langmuir and Melchoir, 1985; Miller et al., 1985; Krest et al., 1999; Sturchio et al., 2001). The physical process known as alpha-recoil, during which the newly created progeny radionuclide recoils in the opposite direction of the ejected alpha particle may liberate Ra rapidly relative to leaching by the weathering process (Tricca et al., 2001; Reynolds et al., 2003). The energy associated with this recoil is 10^4–10^6-times larger than typical chemical-bond energies (Fleischer, 1980; Tanner, 1964). Therefore, isotopes of Ra can be continuously released to ground water by alpha-recoil mechanisms from mineral surfaces.

1.2. Previous national and local radium occurrence surveys

The USEPA has sponsored National Ra- or radionuclide-occurrence surveys for public water-supply systems that use ground-water sources (Hess et al., 1985; Longtin, 1988; Focazio et al., 2001). Results of the randomly designed National Inorganics and Radionuclide Survey (NIRS; see Longtin, 1988) showed that the MCL was exceeded by ^{226}Ra alone in about 1.0% of the 990 raw and finished public (ground) water-supply samples collected. Of these sites, concentrations of ^{226}Ra equaled or exceeded the minimum reporting level (MRL) of that study of 0.0067 Bq/L (0.18 pCi/L) in 40.2% of the samples. The median national concentration for the samples with concentrations greater than the MRL was 0.0144 Bq/L (0.39 pCi/L) and the maximum was 0.559 Bq/L (15.1 pCi/L). Concentrations of ^{228}Ra exceeded 0.037 Bq/L (1 pCi/L), 0.074 Bq/L (2 pCi/L), and 0.185 Bq/L (5 pCi/L) in 12, 2.2, and 0.50% of the samples (Longtin, 1988), and the maximum concentration was 0.448 Bq/L (12.1 pCi/L). Hess et al. (1985) reported a small number of samples in their survey had combined Ra concentrations of about 0.96–1.0 Bq/L (26–27 pCi/L). Focazio et al. (2001) identified (for samples of raw (untreated) ground water from randomly selected public-supply wells) slightly higher maximum concentrations (^{226}Ra, 0.625 Bq/L or 16.9 pCi/L; ^{228}Ra, 1.35 Bq/L or 36.4 pCi/L) in Ra-rich areas for aquifer systems located mostly in the eastern and central USA, though the median concentration determined for ^{226}Ra was identical to that found in the NIRS study. High concentrations were also determined for ^{224}Ra from a small number of public and private supply wells.

Data from multiple local sources have been collected and were summarized by Michel and Cothern (1986) and Zapecza and Szabo (1987). In the eastern USA, local studies have found Ra-rich waters occasionally in the Appalachian province in anoxic waters from black shales and arkoses within Mesozoic Basins (Szabo and Zapecza, 1991), and in acidic waters from orthoquartzites in the Valley and Ridge Province (Senior and Vogel, 1995; Sloto, 2000). Studies have found Ra-rich water derived from the Cretaceous age unconsolidated quartzose sand aquifer systems of the Southeastern Atlantic Coastal Plain in South Carolina and Georgia (King et al., 1982; Focazio et al., 2001), further studies of Cretaceous, Miocene and younger age surficial aquifer systems in the North Atlantic Coastal Plain from Maryland to New Jersey (Bolton, 2000; Szabo et al., 1997, 2005) found the Ra-rich water to be strongly acidic. The presence of high concentrations of short-lived ^{224}Ra in waters from these aquifers indicates the source of the Ra must be the aquifer materials (Szabo et al., 2005). Occurrence of elevated Ra has been noted locally in supply wells that intercept lenses of mineralized or saline waters from aquifer systems of the Gulf Coastal Plain (Cech et al., 1987), and locally in the carbonate Floridan aquifer system (Miller et al., 1985). High concentrations of U and ^{222}Rn have been documented from the waters from the crystalline-rock and glacial sand and gravel aquifer systems (Ayotte et al., 2007), but the regional occurrence or distribution of Ra has not been studied in either, except to evaluate recoil of Ra in glacial sand and gravel aquifers on Long Island (Tricca et al., 2001) and adsorption of Ra to rocks of the region (Krishnaswami et al., 1982). In the central USA, high concentrations especially of ^{226}Ra, but also of ^{228}Ra have been shown to occur in water from the anoxic and somewhat mineralized Midcontinent and Ozark Plateau Cambro-Ordovician dolomite–sandstone aquifer systems from Oklahoma to Minnesota (Gilkeson and Cowart, 1987; Focazio et al., 2001; Sturchio et al., 2001; Grundl and Cape, 2006), and also in the associated Cretaceous sandstones (Kriege and Hahne, 1992).

Areas in the western USA were ranked as having medium to high probability of containing elevated concentration of ^{228}Ra in ground water by Michel and Cothern (1986), but initial studies of Ra occurrence were mainly associated with mine waste (Kaufmann et al., 1976; Landa et al., 1991; Martin and Akber, 1999). In recent drinking water supply studies, ^{226}Ra has been found locally in high concentrations in water from valley-fill sedimentary aquifers from small and large fault-block basins (Ruberu et al., 2005), including some in organic-C -rich basin-fill sedimentary aquifers (Thomas et al., 1993), and on occasion, from deep confined aquifers with anoxic waters (Herczeg et al., 1988; Reynolds et al., 2003). Measurable to high concentrations of ^{224}Ra have on occasion been documented in local aquifers (Sturchio et al., 1993; Focazio et al., 2001; Ruberu et al., 2005).

2. Methods

2.1. Principal aquifer system classifications and descriptions

The sampled wells were distributed in 15 principal or other major aquifer systems (termed PAs) that extend over much of the USA as shown in Fig. 1 (available in color, Online Supplemental Fig. S-1). The PAs initially identified as part of the USGS NAWQA Program (Lapham et al., 2005) account for about 75% of the estimated withdrawals of ground water for drinking-water supply in the USA and were the primary focus of sampling efforts. The 15 PA groupings used in this article differ to a small degree from the classification of Lapham et al. (2005) however because for data-reduction and classification purposes, some of the PAs were combined on the basis of geologic similarity, geologic age, geographic proximity, and similarity of other natural features, and Ra concentration results from some less productive aquifers were included in the final data set. The broader geological classification of DeSimone (2009) was used to classify the 15 PAs into eight geological groups: coastal plain unconsolidated quartzose sands, arkosic and lithic-fragment rich unconsolidated basin fill and alluvium, glacial sand and gravel deposits, sandstones and shales, interbedded (mixed) sandstone and carbonate rocks, carbonate rocks, felsic to intermediate crystalline rocks plus metasediments, and basalts, as shown in Table 1, where brief descriptions from the sampled areas are provided. (For broader descriptions, see the Supplemental Information, and also the National Atlas, USGS, 2005.) Abbreviations shown for PAs in Table 1 are used hereafter). The most areally extensive PA is the glacial sand and gravel system (GLCL), which extends across the northern USA from Maine to Washington (broadly described by Warner and Arnold (2005) and Arnold et al. (2008)).

The broad range of radionuclide contents (^{40}K, equivalent ^{238}U and equivalent ^{232}Th) of the near-surface sediments of the PAs (Table 1) was interpolated in a generalized fashion from the national terrestrial gamma-ray spectral emission maps constructed from measurements during aerial overflights of the USA in the late 1970s as part of the USGS National Uranium Resource Evaluation (NURE) Program (Duval and Riggle, 1999). Although ground water rarely resides in the upper 25 cm that produces the detected gamma rays, the gamma emissions of the surficial materials can indicate the general presence of radionuclide-enriched rock material that might also be present in the subsurface. The ranges of concentrations of ^{222}Rn for the wells sampled for this study from the PAs are also presented in Table 1 as a measure of general lithological radioactivity (Tanner, 1964). The two different measures were found to correlate for felsic crystalline rock and for glacial sand and gravel aquifer systems in the northeastern USA by Ayotte et al. (2007).

2.2. Well selection

The well selection focused on providing the most areally extensive assessment of Ra occurrence among the PAs. A minimum of 30 samples were collected and analyzed for at least one isotope of Ra from each PA. Given its wide extent, the GLCL PA was sampled most (417 samples). Wells were generally sampled once for Ra analysis, primarily (83%) in the 9-a period of intensive study from 1997 to 2005. For the small subset of wells from where more than one sample was collected, the most recent Ra analysis result was used in the nationwide distribution analysis. For several PAs, no well sites, or only half the sites, were sampled and analyzed for the ^{224}Ra isotope.

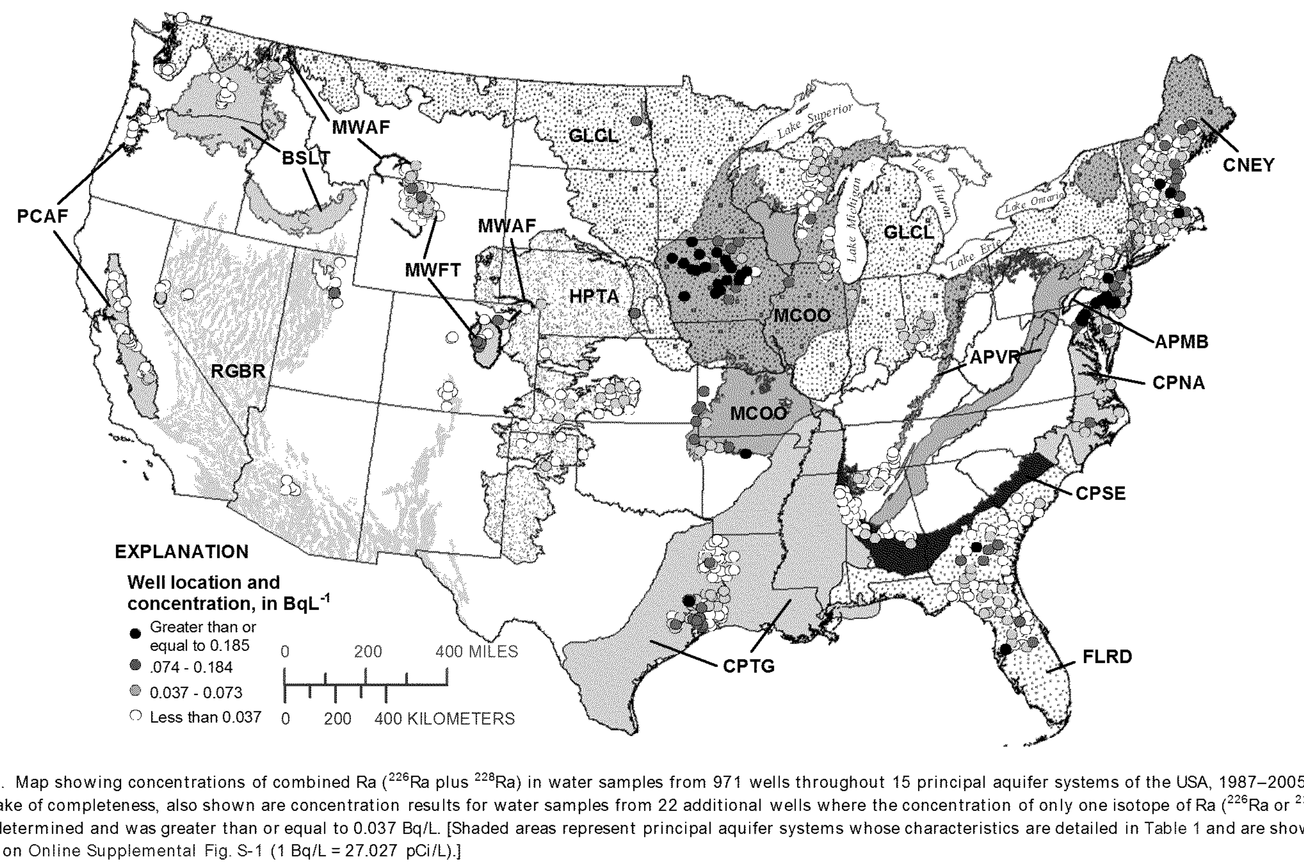

Fig. 1. Map showing concentrations of combined Ra (^{226}Ra plus ^{228}Ra) in water samples from 971 wells throughout 15 principal aquifer systems of the USA, 1987–2005. For the sake of completeness, also shown are concentration results for water samples from 22 additional wells where the concentration of only one isotope of Ra (^{226}Ra or ^{228}Ra) was determined and was greater than or equal to 0.037 Bq/L. [Shaded areas represent principal aquifer systems whose characteristics are detailed in Table 1 and are shown in color on Online Supplemental Fig. S-1 (1 Bq/L = 27.027 pCi/L).]

Table 1

General lithologic, radiologic, and water-quality characteristics of the 15 principal and other major aquifer systems in the USA evaluated in this study, 1987–2005, and distribution of the 1270 sampled wells by water use [eppm, equivalent parts per million from aerial gamma survey; 1 Bq/L = 27.027 pCi/L. Well type: PS, public supply; D, domestic; O, observation; well type was not recorded at some sites. Anoxic redox group, concentration of DO < 1.0 mg/L and one additional criterion: $FeHSO_4$, Fe > 0.1 mg/L and SO_4 6 4 mg/L; $FeLSO_4$, Fe 6 0.1 mg/L and SO_4 6 4 mg/L; Mn, Mn 6 0.05 mg/L and Fe 6 0.1 mg/L; NO_3, NO_3 > 0.2 mg/L, Mn 6 0.05 mg/L and Fe 6 0.1 mg/L; suboxic, NO_3 6 0.2 mg/L, Mn 6 0.05 mg/L, and Fe 6 0.1 mg/L. Mixed redox group, $MixO_2$–Mn, concentration of DO > 1.0 mg/L and Mn > 0.05 mg/L and Fe 6 0.1 mg/L. Bold, greatest median value; italics, smallest median value].

Principal aquifer system name (Code)[1]	States with samples	Predominant lithologies[2]	Indicators: radioactivity concentration		General water quality[2]				Number and type of wells (PS/D[4]/O[5])
					Median and range			Frequency of DO 6 1-mg/L cut-point (%), and common anoxic redox group (s)[3]	
			Range, surficial equivalent U/Th (eppm)[2]	^{222}Radon, median[2], and maximum (Bq/L) [pCi/L]	SC (μS/cm)	pH (standard units)	DO (mg/L)		
Coastal Plain sands; commonly quartzose									
Coastal Plain: North Atlantic (CPNA)	DE, MD, NC, NJ, VA	Sand and clay, some mixed w. gravel or silt	0.1–2.5/0.2–3.5	6.3 [170], 24.8 [670]	177, 17–4210	5.6, 4.0–8.0	3.0, 60.1–13.8	31.0, $FeHSO_4$	24/25/36
Coastal Plain: Southeastern (CPSE)	AL, MS	Sand and clay, some mixed w. gravel	1.5–3.0/2.0–3.5	7.8 [212], 23.0 [623]	58, 12–843	5.4, 4.7–8.3	5.2, 60.1–9.3	33.0, $FeLSO_4$	0/27/3
Coastal Plain: Texas Uplands, Gulf Lowlands, Mississippi Embayment (CPTG)	AR, LA, MO, MS, TN, TX	Sand and clay, some mixed w. gravel; some silt and clayey silt	0.5–2.5/1.5–3.5	11.8 [320], 321 [8670]	490, 40–1980	7.2, 4.4–8.7	0.6, 60.1–9.1	63.2, $FeHSO_4$, suboxic	19/75/30
Basin-fill, alluvial, or fluvial sands and gravels; commonly arkosic or lithic-fragment rich									
High Plains, Tertiary alluvium, fill (HPTA)	KS, NE, OK, TX	Sand and gravel; some sand and clay, sand, or clay	1.0–3.0/2.0–4.0	12.5 [339], 38.8 [1048]	562, 173–2740	7.4, 5.8–8.7	4.6, 60.1–8.3	33.3, $FeHSO_4$, Mn	17/19/27
Mountain West: alluvium, valley fill (MWAF)	CO, ID, MT, WA, WY	Gravel, poorly sorted, mixed w. sand, silt; or sand, poorly sorted, mixed w. gravel and clay; cobbles; some silt, clay	0.5–4.0/1.0–4.5	20.6 [556], 50.3 [1360]	1025, 140–21,500	7.3, 6.5–8.0	3.9, 0.3–10.9	32.6, $FeHSO_4$, Mn, $MixO_2$–Mn	1/1/44
Pacific Coastal, (Central Valley, Willamette Basin) alluvium, fill (PCAF)	CA, OR	Gravel, mixed w. sand, silt; or some sand, mixed w. silt	0.1–3.5/0.5–4.5	22.2 [600], 88.8 [2400]	490, 100–4420	7.4, 6.7–8.4	3.5, 60.1–9.2	23.6, NO_3	1/24/30
Rio Grande and Basin and Range basin fill (RGBR)	AZ, CO, NV, UT	Sand and gravel, mixed w. clay; or gravel and sand, mixed w. silt; cobbles; or sand, silt, clay	2.0–P4.5/3.0–P10	26.7 [723], 181 [4900]	535, 92–37,800	7.2, 6.4–8.9	4.2, 0.2–8.4	15.0, NO_3	11/9/21
Glacial sands and gravels; commonly lithic-fragment rich									
Glacial sand and gravel (GLCL)	17 states[6]	Sand; or gravel; or sand and gravel, some mixed w. silt or clay; some silt or clay	0.1–3.0/0.1–3.5	13.3 [360], 317 [8570]	462, 39–5140	7.2, 4.5–9.1	1.1, 60.1–12.3	49.2, $FeHSO_4$, $MixO_2$–Mn	42/196/179
Sandstones and shales									
Appalachian Piedmont: Mesozoic Basins (APMB)	NJ, PA	Shale, mudstone; or shale and sandstone; or some conglomerate; or argillite	2.5–4.5/2.5–P5	67.3 [1820], 185 [5010]	405, 192–709	7.4, 5.6–8.0	4.2, 0.2–8.2	20.7, Mn, NO_3	1/27/2
Mountain West Foreland/Tertiary/Cretaceous sandstones (MWFT)	CO, MN, MT, ND, WY	Sandstone, some arkosic; some interbedded w. shale; some mostly shaley; or shale	1.0–4.0/2.0–>5	22.2 [600], 164 [4420]	1920, 607–14,490	7.9, 6.2–9.3	0.2, 60.1–8.0	64.9, suboxic, $FeHSO_4$, NO_3	0/24/16
Intermixed sandstones and carbonate rocks									
Appalachian Plateau: Valley and Ridge and Mississipian Limestones (APVR)	AL, PA, TN	Shale; some interbedded w. sandstone, siltstone; or limestone, some w. chert; or residuum; or rare sandstone	1.0–4.5/1.0–≥5	33.1 [896], 223 [6020]	188, 18–1500	6.8, 4.5–8.0	5.2, 0.1–11.6	13.8, $FeHSO_4$	4/35/20
Carbonate rocks									
Floridan, and Surficial (FLRD)	FL, GA, NC, SC	Limestone; or limey sand	0.1–3.0/0.2–4.0	15.9 [430], 199 [5365]	346, 27–8680	7.4, 6.3–8.5	0.3, 60.1–	71.4, suboxic, $FeHSO_4$, $FeLSO_4$,	4/71/27

(continued on next page)

Table 1 (continued)

Principal aquifer system name (Code)[1]	States with samples	Predominant lithologies[2]	Indicators: radioactivity concentration		General water quality[2]				Number and type of wells (PS/D[4]/O[5])
			Range, surficial equivalent U/Th (eppm)[2]	^{222}Radon, median[2], and maximum (Bq/L) [pCi/L]	Median and range			Frequency of DO6 1-mg/L cut-point (%), and common anoxic redox group (s)[3]	
					SC (l S/ cm)	pH (standard units)	DO (mg/L)		
							8.8	NO_3	
Carbonate rocks (continued)									
Mid-continent and Ozark Plateau Cambro-Ordovician dolostones (MCOO)	AR, IA, KS, MO, OK	Dolomite; or sandstone; or interbedded dolomite and sandstone	Minimal surficial exposure	5.9 [160], 50.7 [1370]	854, 225–2340	7.1, 6.6–7.8	0.3, 60.1–8.4	93.8, $FeHSO_4$, suboxic	48/0/1
Crystalline (felsic to intermediate) igneous and metamorphic rock and basalt									
Crystalline (felsic) rock: New England (CNEY)	CT, MA, ME, NH, RI, VT	Metamorphic or igneous rocks: schist, granite-gneiss, tonalite, granite, syenite	2.0–4.5/3.0–p 10	81.4 [2200], 7955 [215,000]	207, 36–1480	7.6, 5.1–9.3	1.0, 60.1–10.5	53.9, suboxic, $FeHSO_4$	0/87/2
Basalt (BSLT)	CT, HI, ID, WA	Basalt	0.1–1.0/0.1–1.5	4.1 [110], 174 [4700]	340, 42–1460	7.2, 6.3–8.3	7.7, 4.4–9.2	oxic only	30/1/5

[1] Codes used in this report differ slightly from those of Lapham et al. (2005) and DeSimone (2009); classification is discussed in the Online Supplemental Information.
[2] Water quality, general radioactivity, and lithologic information is only for wells from which samples were analyzed for Ra, or includes only the approximate sampled area.
[3] See McMahon and Chapelle (2008) for detailed description. For this report, cut-points for groups were modified as follows: DO, 1 mg/L; NO_3, 0.2 mg/L.
[4] D; Domestic wells, includes commercial, commercial/industrial/fire-protection,and recreational uses.
[5] O; Observation wells, includes irrigation and stock supply wells not used for drinking water in agricultural areas.
[6] Includes 17 states: AK, CT, ID, IL, IN, MA, ME, MI, MN, NH, ND, OH, PA, RI, VT, WA, WI.

Of the 1270 sampled wells, the well-use distribution (202 public drinking-water supply, 621 domestic supply, and 443 shallow observation wells) indicates a slight bias toward oversampling of the shallow resource (Table 1). This bias was acceptable because the focus of the study was the potable shallow resource rather than all water resources (as opposed to Scott and Barker (1962) who did sample deep saline irrigation and stock wells). A limitation shared with previous national surveys (Longtin, 1988; Focazio et al., 2001) was that small water-supply systems relying on ground water in the western USA were least sampled.

2.3. Sample collection

Raw (untreated) samples of water were collected and filtered (0.45 l m) as close to the wellhead as possible after the pump had been running for about 30 min or more and values of measured field properties (water temperature, dissolved-O_2 (DO) content, pH and specific conductance (SC)) were stable (Koterba et al., 1995). The 1 L samples for determination of each Ra isotope to be analyzed were acidified to pH < 2 with ultra-pure HNO_3. Samples were shipped overnight to the analyzing laboratory (USGS National Water Quality Laboratory in Denver, CO; USGS National Research Program Isotope Laboratory in Reston, VA; or contract laboratories). The 122 sequential-replicate and field- and equipment-blank samples were collected randomly using the same procedures as the environmental samples. Not every sample or every replicate sample was analyzed for all the Ra isotopes.

2.4. Analytical methodology

Samples from all but 4 of the 1270 wells were analyzed for ^{226}Ra or ^{228}Ra, mostly using USEPA-approved techniques (Table 2). Alpha spectrometry (Sill et al., 1979; Sill and Williams, 1981; Sill, 1987; Morvan et al., 2001) was the method used to determine the concentration of ^{224}Ra and was the second most common technique used to determine concentrations of ^{226}Ra. The alpha spectrometry focused on alpha radiation emitted at specified energy levels for ^{224}Ra and ^{226}Ra (5.686 and 4.785 million electron volts, respectively). A 100-min count was long enough to typically achieve an expected (pre-defined) minimum detectable concentration (MDC) of about 0.037 Bq/L (1 pCi/L) or less for sample aliquots of up to 1 L. Cation-exchange chromatography (Bio-Rad AG 50W-X8 resin) was used to separate the Ra from the water, which was then eluted with 8-M HNO_3, and was co-precipitated with barite using a seeding suspension to ensure the formation of uniform fine-grained crystals (Sill and Williams, 1981; Sill, 1987; Focazio et al., 2001; Nour et al., 2004; Arndt, 2010). Chemical separation by forming the Ba–Ra–SO_4 precipitate was completed within about 48 h for ^{224}Ra and ^{226}Ra analysis by alpha spectrometry, with counting proceeding immediately thereafter. A radioactive tracer (^{133}Ba) was added to the samples to determine yield and was analyzed by gamma spectroscopy. For a subset of 135 mostly oxic and alkaline water samples collected from the western USA in 2004, the ^{224}Ra was initially extracted for alpha-spectroscopic analysis using Mn-coated fibers (Kim et al., 2001) as the water chemistry (oxic, alkaline) was optimal for this application.

Raw values, including negative values for radionuclides, were reported and are stored in the USGS National Water Inventory System (NWIS) database. Missing raw values are primarily those censored for low concentrations of ^{228}Ra and low gross alpha-particle activity, mostly determined before 1997. Evaluation of measurement performance for single measurements at individual sites used the raw values (Currie, 1968; Troyer et al., 1991; McCurdy et al., 2008).

Water samples from most wells were analyzed for concentrations of U and ^{222}Rn, and for gross alpha- and beta-particle

Table 2
Description of methods for analysis for radionuclides and radioactivity in 1270 water samples from 15 principal aquifer systems in the USA, 1987–2005.[LRL, laboratory reporting level; SSMDC, sample specific minimum detection concentration performance indicator; 1 Bq/L = 27.027 pCi/L.].

Constituent	Number of analyses	Typical range of LRL or SSMDC	Method and EPA method number	Citation
^{226}Radium	528	0.0037–0.0074 Bq/L (0.1–0.2 pCi/L)	Barium-sulfate co-precipitation and ^{222}Radon de-emanation, with Rn cold trapped on charcoal and counted with alpha scintillation (EPA 903.1)	Krieger and Whittaker (1980)
^{226}Radium	143	0.0074–0.0259 Bq/L (0.2–0.7 pCi/L)	Low-background proportional count from planchet after barium sulfate co-precipitation (EPA 903.0)	Krieger and Whittaker (1980)
^{226}Radium	525	0.0074–0.0148 Bq/L (0.2–0.4 pCi/L)	Alpha-spectroscopy counting after barium-sulfate co-precipitation	Sill and Williams (1981), Sill and Olson (1970), Sill (1987)
^{224}Radium	645	0.0111–0.0296 Bq/L (0.3–0.8 pCi/L)	Alpha-spectroscopy counting after either barium-sulfate co-precipitation or manganese-fiber extraction	Sill et al. (1979), Sill and Williams (1981), Kim et al. (2001)
^{228}Radium	1042	0.01295–0.0296 Bq/L (0.35–0.8 pCi/L)	Low-background proportional beta counting of ^{228}Ac ingrowth after Barium co-precipitation (EPA 904.0)	Krieger and Whittaker (1980)
Gross alpha and beta (48–72-h holding time or conventionalwith no holding time and 30 days or more elapsed time permissible before analysis)	765 (135 with 72-h holding time)	About 0.0925–0.148 Bq/L (2.5–4 pCi/L)	Low-background proportional count after evaporation for low dissolved solids ground water (EPA 900.0)(ASTM, 1999), or after co-precipitation for high dissolved solids samples or brine (EPA 900.1) using ^{230}Th and ^{137}Cs as the standards	Krieger and Whittaker (1980), Parsa (1998), ASTM (1999)
Uranium (mass)	1237	0.1–1.0 Ig/L	Inductively coupled plasma-mass spectrometry (EPA 200.8)	Faires (1993)
^{222}Radon	1135	1.48–2.59 Bq/L (40–70 pCi/L)	Liquid scintillation (EPA 913.0)	Pritchard and Gesell (1977)

activities (Table 2), with the gross alpha-particle activity determined within a 48–72-h holding time (Parsa, 1998) for 135 samples collected in 2004. Samples from all but two of the 1270 wells were analyzed for a suite of major and trace inorganic chemical constituents using standard techniques (Faires, 1993; Fishman and Friedman, 1989).

2.5. Quality assurance and limitations of the analytical methods

Because a large data set collected over more than 15 a is evaluated in this study, conservative interpretations of data-quality criteria were applied. The sample-specific minimum detectable concentration (SSMDC) "performance indicator" was determined on the basis of instrument operating conditions at the time of measurement, and is typically twice the magnitude of the critical level for detection (Currie, 1968). The SSMDC was used as a conservative criterion to evaluate raw, unrounded values with respect to whether they were considered to be a detectable and a suitably quantifiable concentration. Radionuclide concentration values less than the SSMDC were considered too low in concentration for satisfactory quantification within performance expectations, and were conservatively equated with non-detection.

The quality-assurance data and performance criteria collected in this study indicate that, for the analytical techniques used, there were limitations to precise quantification and detection for ^{224}Ra and ^{228}Ra at concentration ranges of 0.011 to about 0.030 Bq/L (0.3–0.8 pCi/L) that are typical of many environmental samples (Online Supplemental Table S-1). The 0.030–0.037-Bq/L level is reasonable for assuming detection for ^{224}Ra and ^{228}Ra. Concentrations of ^{226}Ra when determined by the Rn de-emanation technique were quantifiable, precise, and reproducible at levels P 0.0037 Bq/L (0.1 pCi/L), and at about levels 0.011 Bq/L when determined by alpha spectroscopy. Beta particles are more difficult to detect than alpha particles and the background count cannot be maintained at levels as low as those achievable for measurement of alpha particles; thus, the measurement of ^{228}Ra by the beta-counting technique was typically more imprecise and had more difficulty in meeting the (pre-determined) MDC of 0.037 Bq/L than the measurement of ^{226}Ra, an observation that is consistent with those of previous studies (Cothern et al., 1984; Focazio et al., 2001). The resulting disparity in performance is a limitation of the analytical approach. Detections of ^{224}Ra in equipment blank samples are assumed to indicate analytical "noise" in the laboratory associated with occasional poor performance of the alpha-spectrometric technique for ^{224}Ra analysis because ^{226}Ra and ^{228}Ra were not detected in equipment blanks. Data for replicate samples indicate the analytical results are reproducible within the bounds of the precision estimate performance constraints of the analytical techniques (about ± 22 ± 25% for ^{226}Ra and ^{228}Ra), though uncertainty was largest for ^{224}Ra analysis (near±34%; Online Supplemental Table S-2).

2.6. Data analysis

The Ra concentration data set is limited by quantification issues at the low end of concentrations and a long tail of high-end concentrations, and the use of non-parametric (rank transform) statistics was most appropriate (Helsel and Hirsch, 1992). The significance level for all the non-parametric statistical tests was set equal to 0.05. Concentrations lower than the SSMDC including reported negative values were assigned a uniform minimum value that was less than the smallest Ra isotope value detected at a concentration that was greater than the associated SSMDC (^{224}Ra, 0.002 Bq/L (0.054 pCi/L), ^{226}Ra, 0.0005 Bq/L (0.014 pCi/L), and ^{228}Ra, 0.013 Bq/L (0.37 pCi/L)) before ranking for non-parametric statistical tests. For the small number of Ra analyses, mostly but not exclusively for ^{228}Ra for which a censored result (commonly the 0.037 Bq/L MDC) was reported, the censored results were similarly treated as a uniform minimum value, but were set less than the smallest detected Ra isotope. For ^{228}Ra, 0.0037 Bq/L (0.101 pCi/L) was used. For plotting Ra isotope population distributions in "boxplot" format and for use with the non-parametric statistics, the same lowest ranked values that represented concentrations less than the SSMDC were used. No other manipulation, censoring, or screening of the raw-data values was attempted in order to avoid biases resulting from the omission of low concentrations that might change the true statistical distribution of the population of Ra-concentration data (Helsel and Hirsch, 1992). In a similar fashion, for each ancillary chemical constituent, the highest laboratory reporting level (LRL) was determined, and the Spearman correlation coefficients were calculated with the results less than any of the LRLs ranked equally as the lowest value. For the wells sampled for determination of Ra concentration, about 50% and 1% of the results were below the highest LRL for U and ^{222}Rn, respectively (1 l g/L and 2.59 Bq/L (70 pCi/L), respectively). For Ra, the raw, unrounded values of concentrations were used to compute standard distributional statistics for the entire data set and for subgroups even if the concentrations were lower than the SSMDC. The standard distributional statistics were also computed for the SSMDC values to provide a measure of the degree of overlap among the population distributions and thereby assess the general level of confidence in the results.

The non-parametric group-comparison tests, the Kruskal–Wallis and Tukey–Kramer test, were used to identify which group means significantly differed in Ra concentration distributions from among the groups of data (Helsel and Hirsch, 1992). The differences among the higher and lower ranked group reflect the difference in the central tendencies of the population distribution of the groups about the mean rank, but do not necessarily indicate the group that has the highest individual concentration. Classification groups included the PAs and groups of PAs (combined surrogate for geology and hydrology) and specific geochemical-classification groups. Results were ranked and coded sequentially, with the group with the highest mean of ranks coded "A", the group with the next highest mean ranks was coded "B", then "C", and so on; overlapping groups were coded with the letter for each overlapping group, "BC", for example, or "BD", representing overlap with groups B and C, and B, C, and D, respectively. To simplify representation of overlapping groups in data tables, only the first and last letters of the range of overlapping groups are listed.

Principal components analysis (PCA) was used to reduce the dimensionality of the multiple correlations determined among the concentrations of Ra and other chemical constituents. The individual explanatory variables (constituent concentrations) are represented by loadings into individual principal components; the highest loadings are attributed to the explanatory variables that account for the most variance within the individual principal component. The first principal component accounts for as much variation in the data set as possible. Each successive component attempts to account for the data variance not explained by previous components. The 22 constituents included in the analysis (major ions, selected trace elements, and water properties) were measured in at least 85% of the samples. The concentrations of Sr, an alkali-earth trace cation, were not included in the analysis despite strong correlation with concentrations of Ra in nearly all PAs because Sr was analyzed in only 61.5% of samples. Concentrations were normalized by converting to logarithmic values. Rotations were not applied as variance of the data set was much larger than analytical error or variance within individual explanatory variable populations.

The statistically most significant component with which combined Ra concentration was correlated most strongly was determined for this study. The typical loading coefficient values, (r) for combined Ra, were P [0.20–0.40], with the absolute values of the coefficients represented with brackets; the full range of the loading coefficient values considered were [0.126–0.433] for the entire data set, and for individual PAs. The minimum eigenvalue for any component considered initially was 2.0; two reported components with values as low as 1.34 were included after further consideration. A limitation important to note is that a given principal component may be indicative of more than one geochemical factor. Further, any one component, or even a group of components, may not be exhaustive of all possible geochemical conditions in which Ra might be present within a given PA, and the significance of lesser components were not evaluated. The non-parametric Spearman's rank correlation test was used to characterize relationships among the Ra radionuclide concentrations and the concentrations of ancillary chemical constituents for the overall data set and for the PAs and geochemical groups to further delineate specific geochemical relationships.

Ratios of radionuclide concentrations were determined using raw values only when concentrations were greater than their respective SSMDCs. Ratios may have substantial bias when the raw concentrations used are below the SSMDC. The difference in performance of the analytical techniques for the Ra isotopes likely results in potential positive population bias for tabulations of ^{228}Ra/^{226}Ra activity ratios, for example (see discussion in the Online Supplemental Information), the isotopic ratios are discussed in qualitative fashion, with no statistical tests applied. Because of the analytical limitation, geological groups that had low Ra concentrations were not characterized or were poorly characterized in terms of Ra isotope ratios.

The redox classification of McMahon and Chapelle (2008) was used for general descriptive purposes of PA geochemistry (Table 1). The classification was modified slightly for purposes of describing geochemical environments relating to Ra occurrence in that all samples with DO 6 1 mg/L (instead of DO 6 0.5 mg/L) were considered suboxic or anoxic, and samples with DO 6 1 mg/L and NO_3 concentrations >0.2 mg/L (instead of >0.5 mg/L) were considered NO_3 reducing. Some samples were classified into the anoxic groups that might otherwise have been within the "mixed" redox groups of McMahon and Chapelle (2008), but this slight change in criteria emphasizes the anoxic component. Samples with DO 6 1 mg/L were prevalent in many PAs. Major-ion compositional variability assessment was simplified to characterization of the predominant anion; anion concentrations were converted to (milli)equivalents/L (Back, 1966), and the anion with the highest equivalence was determined to be predominant. Thermodynamic calculations of water sample saturation with respect to barite (solubility product $10^{ffi9.97}$) were completed using a spreadsheet with appropriate chemical activity factors and were spot-checked with the geochemical modeling program PHREEQEC (Parkhurst and Appelo, 1999). Minor high bias was occasionally noted for spreadsheet results likely because of underestimation of ion activity coefficients and complexation of species.

3. Radium occurrence in the water from the principal aquifer systems

3.1. Combined radium (sum of ^{226}Ra plus ^{228}Ra)

Concentrations of combined Ra in 39 (4.02%) of the 971 water samples for which both ^{226}Ra and ^{228}Ra concentrations were determined and summed were equal to or greater than the MCL (Figs. 1 and 2; Online Supplemental Table S-3). Of the 39 wells where the combined Ra concentrations were greater than the MCL, ^{226}Ra was the larger of the two isotopes in 21 (54%). This frequency of occurrence of concentrations of ^{228}Ra plus ^{226}Ra greater than the USEPA MCL is consistent with the general level of frequency of occurrence in excess of the respective MCLs for other important trace element constituents collected throughout the PAs in the USA, including U and As (1.7% and 6.8% frequency, respectively, in samples from domestic wells; DeSimone, 2009). Concentrations of combined Ra were greater than or equal to 0.148 Bq/L (4 pCi/L), 0.111 Bq/L (3 pCi/L), and 0.037 Bq/L (1 pCi/L) for 50 (5.15%), 63

(6.49%), and 260 (26.8%), respectively, of the 971 samples for which both ^{226}Ra and ^{228}Ra concentrations were measured (Online Supplemental Table S-3). When considering the larger data set of the 1266 water samples analyzed for one or both of these Ra radioisotopes, 40 (3.16%) were equal to or greater than the MCL, because in one sample the ^{226}Ra concentration alone exceeded the MCL but the concentration of ^{228}Ra was not measured, and concentrations exceeded 0.148 Bq/L for a total of 52 (4.10%) of the 1266 samples.

Concentrations of combined Ra greater than the MCL were mostly found in the eastern and central USA (Fig. 1). The maximum concentration of combined Ra was 0.752 Bq/L (20.4 pCi/L) in water from the Coastal Plain-North Atlantic PA. The combined-Ra MCL was exceeded in 7 PAs, listed in decreasing order of frequency of occurrence: Midcontinent and Ozark Plateau Cambro-Ordovician dolomites and sandstones (MCOO), Coastal Plain-North Atlantic quartzose sand (CPNA), Floridan (phosphatic) limestone (FLRD), felsic crystalline rock (granitic, metamorphic) in New England (CNEY), Appalachian Piedmont-Mesozoic Basins (APMB), Coastal Plain-Texas uplands-Gulf Coast Lowlands-Mississippi Embayment (CPTG), and glacial sands and gravels (GLCL) (Figs. 1 and 2; Online Supplemental Table S-3). Of the 8 broad geological groups (Table 1), the concentrations of combined Ra greater than the MCL were found in 5, listed in decreasing order of frequency of occurrence: carbonate rocks, quartzose coastal sands, lithified sandstones and shales, crystalline felsic rocks, and glacial sands and gravels.

The result of the Tukey–Kramer group comparison tests for the PAs (Table 3) indicate that for concentrations of combined Ra, 4 PAs are grouped sequentially as having the highest mean ranks (Group A and overlapping groups): the MCOO, the CPNA, the FLRD, and the Mountain West Foreland Basin Tertiary and Cretaceous sandstones (MWFT). These 4 PAs have combined-Ra concentrations P 0.037 Bq/L in more than 35% of the samples, including in 87% and 67% of the samples from the MCOO and CPNA PAs, respectively. Concentrations of combined Ra were greater than or equal to the MCL in more than 63%, 20% and 4.4% of the samples from the MCOO, CPNA, and FLRD PAs, respectively (Figs. 1 and 2), and were greater than or equal to 0.148 Bq/L in 73% and in 28% of the samples from the MCOO and CPNA PAs, respectively. No sample exceeded the combined Ra MCL from the MWFT PA, but concentrations exceeded 0.074 Bq/L in 12.9% of samples.

Six PAs formed the group with the next (second) highest mean ranks (Tukey–Kramer groups, B and overlapping groups): the CNEY, APMB, CPTG, GLCL, High Plains Tertiary alluvium (HPTA), and Coastal Plain – Southeastern (CPSE). The second-tier group includes the remaining 4 PAs with at least one sample with combined Ra concentration greater than the MCL. More than 25% of the samples for three of these PAs (CNEY, CPTG, HPTA) have a combined-Ra concentration P 0.037 Bq/L, and the frequency of such samples was 23.3% for the APMB PA (Fig. 2; Online Supplemental Table S-3).

The basalt (BSLT) PA has the lowest mean rank and only one sample contained combined Ra at a concentration P 0.037 Bq/L. The Appalachian Plateau Valley and Ridge and Mississippian limestones (APVR), Pacific Coastal alluvium and fill (PCAF), Mountain West alluvium and fill (MWAF), and Rio Grande-Basin and Range (RGBR) PAs have the next-to-lowest mean ranks, but cannot be statistically distinguished from the PAs whose mean ranks also are among the next highest group. For these 4 PAs, combined-Ra concentrations P 0.037 Bq/L occurred with low frequency (5.1–21.4%).

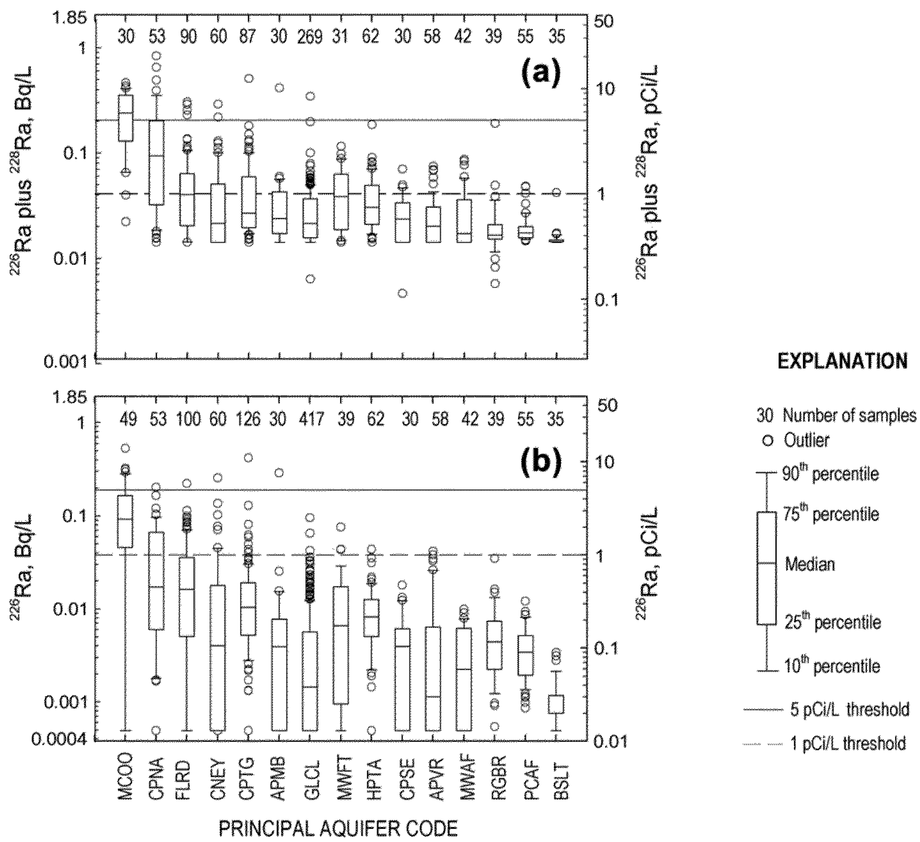

Fig. 2. Boxplots showing concentrations of (a) ^{226}Ra plus ^{228}Ra, and (b) ^{226}Ra, grouped by principal aquifer systems of the USA in decreasing order of ^{226}Ra concentration, 1987–2005. Note that for plotting purposes, values for ^{228}Ra concentration were censored below the lowest detectable concentration that satisfactorily met performance criteria. The number of samples is indicated above the boxplots. [Principal aquifer abbreviations and descriptions are provided in Table 1 and locations are shown in Fig. 1.]

Table 3
Differences in Ra concentration by geochemical conditions (pH and redox and dominant anion) and geology (principal aquifer and matrix type) as determined by the Tukey–Kramer statistical test for 1270 water samples from 15 principal aquifer systems in the USA, 1987–2005. [BOLD, highest group; –, no differences; N, no analyses. Group code sequence: highest mean of ranks is "A", next highest mean ranks, "B", then "C", and so on; overlapping groups include the letters for each overlapping group (examples: "BC" and "BD" represent overlap with groups B and C, and B, C, and D, respectively).]

Group	^{226}Radium + ^{228}Radium	^{226}Radium	^{228}Radium	^{224}Radium	Uranium	^{222}Radon
Grouping by pH and redox as delimited by concentration of dissolved oxygen (DO) in mg/L						
pH 6 6; DO P 1	A	A	A	–	C	A
pH 6 6;DO < 1	A	A	AB	–	C	B
pH > 6;DO < 1	A	A	B	–	B	B
pH > 6;DO P 1	B	B	B	–	A	A
Grouping by predominant anion						
Sulfate	A	A	A	A	A	–
Nitrate	AB	AB	A	A	C	–
Chloride	B	B	B	B	C	–
Bicarbonate	B	B	B	B	B	–
Grouping by principal aquifer code						
MCOO	A	A	A	N	CE	GI
CPNA	AB	AB	B	A[a]	DG	GI
FLRD	AC	AC	BE	BD[a,b]	CD	CF
MWFT	AD	AE	B	AB	BD	BE
CPTG	BD	AC	B	AC[a]	DF	FH
HPTA	BD	AD	B	AC	AB	DG
APMB	BE	BG	BC	BD[b]	AC	AB
CNEY	BE	BF	BE	AD[b]	BD	A
GLCL	BE	EG	BD	BD[a,b]	CD	CF
CPSE	BE	DG	BD	BD	EG	FI
APVR	CE	DG	BE	BD[b]	EG	BC
MWAF	CF	DG	BE	A	A	BE
PCAF	CF	CG	BE	A[a]	AB	BD
RGBR	CF	BF	BE	AB	A	AC
BSLT	DF	EG	BE	BD[a,b]	DG	GI
Grouping by predominant aquifer matrix type						
Carbonate rocks	A	A	AB	CD[a,b]	C	D
Coastal Plain sands	BC	B	A	AC	D	D
Sandstones	BC	C	A	AD	B	B
Crystalline	BD	C	AC	BD[b]	B	A
Glacial sands	BD	D	AB	BD[a,b]	C	C
Alluvial sands	CD	C	AC	AB	A	B
Sandstone/carbonate	CD	CD	AC	CD[b]	D	B
Basalt	E	D	AC	BD[a,b]	D	E

[a] The ^{224}Ra radionuclide not analyzed in about 50% or more of samples.
[b] More than 65% of ^{224}Ra concentration < sample specific minimum detection concentration (SSMDC).

3.2. Individual radium radionuclide concentrations

Concentrations of ^{226}Ra were greater than or equal to the 0.185 Bq/L MCL in 13 (1.09%) of the 1195 samples analyzed for this isotope, exceeded 0.111 Bq/L in 33 (2.76%) samples, and exceeded 0.037 Bq/L in 105 (8.79%) samples (Online Supplemental Table S-3). In terms of elevated occurrence of the individual ^{226}Ra isotope, 4 PAs, the MCOO, CPNA, FLRD and CPTG tended to have the highest mean rank values, though the mean rank values of two more PAs, those of the MWFT and HPTA also overlapped with the range of the first four (Table 3). The maximum concentration of ^{226}Ra, 0.518 Bq/L (14.0 pCi/L), was measured in water from the MCOO PA. Of the samples in which the ^{226}Ra concentrations were greater than or equal to the MCL, more than half were from the MCOO PA. Concentrations of ^{226}Ra were greater than 0.037 Bq/L in 79.6% of the samples from the MCOO, in 37.7% of the samples from the CPNA, and in 22.0% of the samples from the FLRD PA.

Concentrations of ^{228}Ra were greater than 0.185 Bq/L in 8 (0.77%) of the 1042 samples analyzed for this isotope. Concentrations exceeded 0.037 Bq/L in 147 (14.1%) samples, 0.074 Bq/L in 47 (4.51%), and exceeded 0.111 Bq/L in 23 (2.21%). The MCOO PA had the highest overall mean rank concentration for ^{228}Ra, with 4 PAs, the CPNA, CPTG, MWFT and HPTA, forming the group with the next highest values (Table 3). All the remaining groups of PAs had population distributions about the mean rank that were lower than, but in terms of statistical significance, overlapped with, that of these 4. The maximum concentration of ^{228}Ra, 0.688 Bq/L (18.6 pCi/L), was measured in water from the CPNA PA. Half of the eight samples in which the concentration of ^{228}Ra was greater than or equal to the MCL were from the CPNA PA, with the FLRD PA and the GLCL PA (in New England) also having concentrations of that magnitude (Fig. 3). The overall concentration distributions for ^{228}Ra and ^{226}Ra are generally similar to that observed for the NIRS study (Longtin, 1988).

Concentrations of ^{224}Ra were greater than or equal to 0.185 Bq/L in two (0.31%) of the 645 samples analyzed for this isotope. Concentrations of ^{224}Ra were greater than or equal to 0.037 Bq/L in 42 (6.51%) samples, and exceeded 0.111 Bq/L in 7 (1.08%) samples (Fig. 3; Online Supplemental Table S-3). The maximum ^{224}Ra concentration of 0.392 Bq/L (10.6 pCi/L) was determined in water from Quaternary alluvial deposits in the Mountain West (MWAF PA) (Fig. 4). In terms of elevated occurrence of the individual ^{224}Ra isotope, the CPNA PA (quartzose sand) had the highest overall mean rank concentration along with the MWAF and PCAF PAs (alluvium and basin fill sands), with three additional PAs, the CPTG, HPTA and MWFT (coastal and fluvial sands, and sandstone) forming the group with the next highest set of concentrations (Table 3). Concentrations of ^{224}Ra were commonly greater than the corresponding SSMDCs in these 6 PAs with the greatest mean ranks. The concentrations of ^{224}Ra exceeded 0.074 Bq/L in the CPNA, MWAF and MWFT PAs in more than 21% of the samples, and exceeded 0.111 Bq/L in 15% of the samples from the CPNA. Of the eight broad

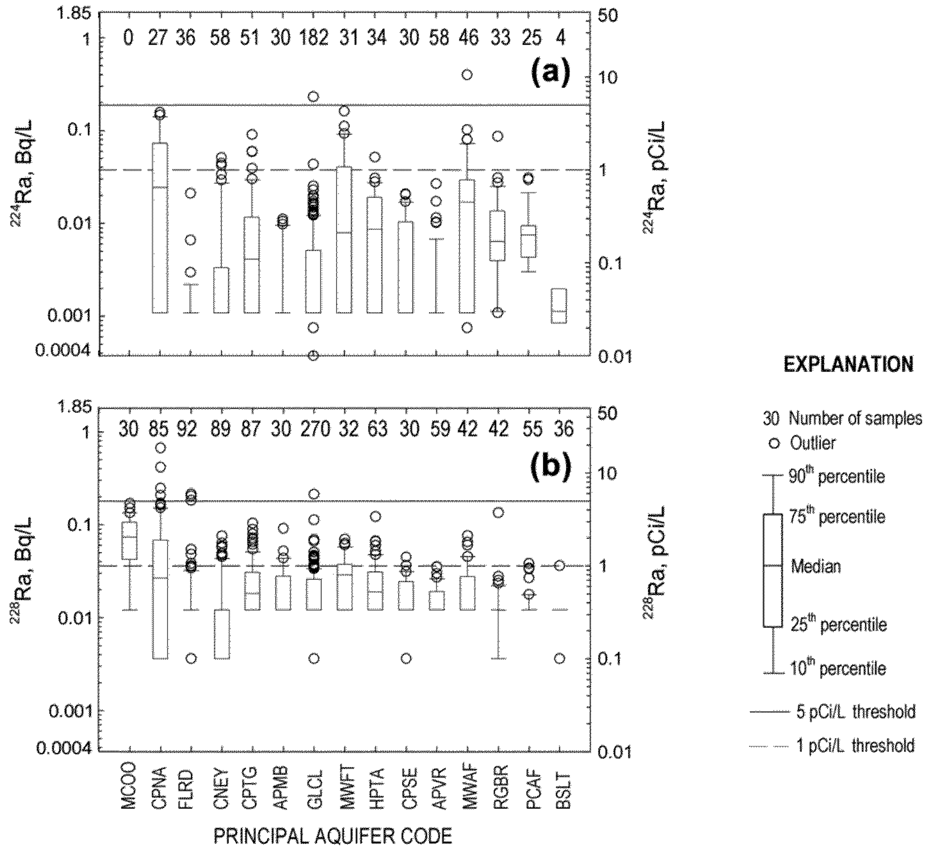

Fig. 3. Boxplots showing concentrations of (a) ^{224}Ra, and (b) ^{228}Ra, grouped by principal aquifer systems of the USA in decreasing order of ^{226}Ra concentration (shown in Fig. 2), 1987–2005. Note that for plotting purposes, values for ^{224}Ra and ^{228}Ra concentration were censored below the lowest detectable concentration that satisfactorily met performance criteria (see text). The number of samples is indicated above the boxplots. [Principal aquifer abbreviations and descriptions are provided in Table 1 and locations are shown in Fig. 1.]

geological groups (Table 1), the highest concentrations of ^{224}Ra were found in sands: the quartzose coastal sands, arkosic and lithic-fragment rich alluvial and basin-fill sands, and lithified sandstones, though the sample distribution did under-represent some of the other lithologic groups. Only 44.9% (172 of 383) samples from 5 PAs (MCOO, CPNA, FLRD, CNEY, and CPTG) with generally the highest concentrations of the other Ra isotopes were analyzed for ^{224}Ra. The cumulative frequency distribution of ^{224}Ra of Focazio et al. (2001) generally indicated greater concentrations than those observed in this study, with about 20% of their samples equaling or exceeding 0.185 Bq/L; many of those samples were, however, from the area of the MCOO PA, and no sample was analyzed for ^{224}Ra concentration from there in this study. The current study may, then, under-report the actual frequency of elevated ^{224}Ra concentration occurrence in terms of the national population distribution because analysis for ^{224}Ra was particularly sparse in some PAs where concentrations of the other Ra isotopes were high.

3.3. Correlations among individual radium radionuclide concentrations

The concentrations of ^{228}Ra correlated significantly and reasonably strongly with those of ^{224}Ra and ^{226}Ra (Spearman's rank correlation coefficient, +0.236 and +0.326, respectively). The concentration ratio of ^{228}Ra/^{226}Ra was variable and the concentrations plotted on a scatter diagram did not cluster closely about a line with a 1:1 slope (Fig. 5). For ^{228}Ra and ^{226}Ra concentrations greater than 0.037 Bq/L, some samples were strongly enriched in one isotope relative to the other, and the individual ^{228}Ra/^{226}Ra ratios ranged widely (from 0.124 to 10.21), and even though some samples did group closely about the 1:1 line, scatter was still substantial. The slope of the best fit line for ^{228}Ra as a function of the ^{226}Ra (activity) concentrations for only those values higher than 0.037 Bq/L was not statistically significant. The generalized slope of the best fit line for samples with both isotope concentrations greater than the associated SSMDCs was 0.35 with an intercept, 0.4 Bq/L (not shown in Fig. 5). The distribution was such that when both radionuclides were detected at concentrations that were less than 0.037 Bq/L, relative differences among concentrations were commonly large and the concentrations of ^{228}Ra were commonly greater than concentrations of ^{226}Ra (Fig. 5). The median ^{228}Ra/^{226}Ra activity (concentration) ratio was 2.58 for all the samples where both concentrations were detectable, but was 1.02 when both detected concentrations were greater than or equal to 0.037 Bq/L. The collected data from this study indicates that the concentration of co-occurring ^{228}Ra cannot be reasonably estimated solely on the basis of the more readily measurable concentration of ^{226}Ra on the national scale. Perhaps in those individual PAs where detection frequencies for both the isotopes are high (listed below), detailed studies may provide assessment of the degree to which the ratios are constrained locally, allowing for possible development of a somewhat more useful "screening" tool using a simple regression model with the concentration result for one isotope to estimate the concentration of the other. Of the 971 samples in which the concentrations of ^{228}Ra and ^{226}Ra were determined, both were greater than the respective SSMDCs in 282 samples (29.0%), with detection and quantification of ^{228}Ra being the limiting factor most often. The concentrations of ^{228}Ra and ^{226}Ra were both greater than the respective SSMDCs in 45% or more of samples from only 4 PAs, listed in order of decreasing frequency: MCOO, CPNA, HPTA, and

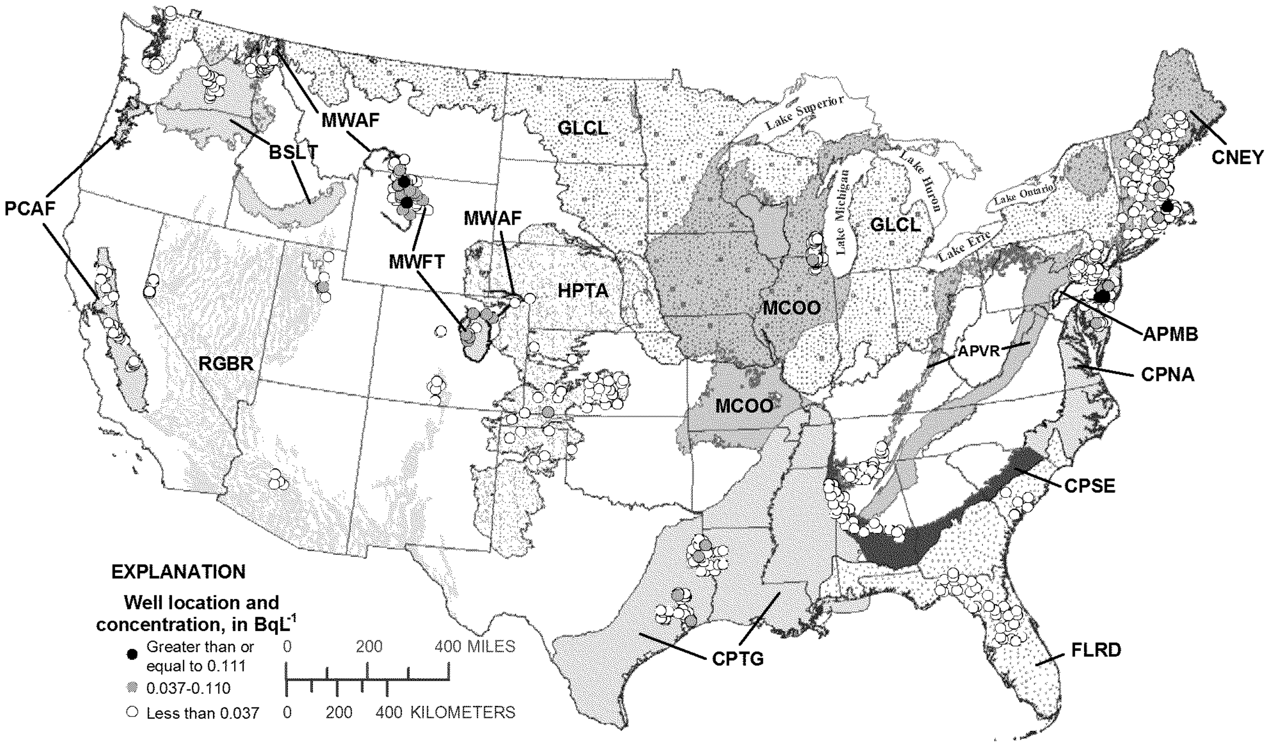

Fig. 4. Map showing concentrations of ^{224}Ra in water samples from 645 wells throughout 15 principal aquifer systems the USA, 1998–2004. [Shaded areas represent principal aquifer systems whose characteristics are detailed in Table 1.]

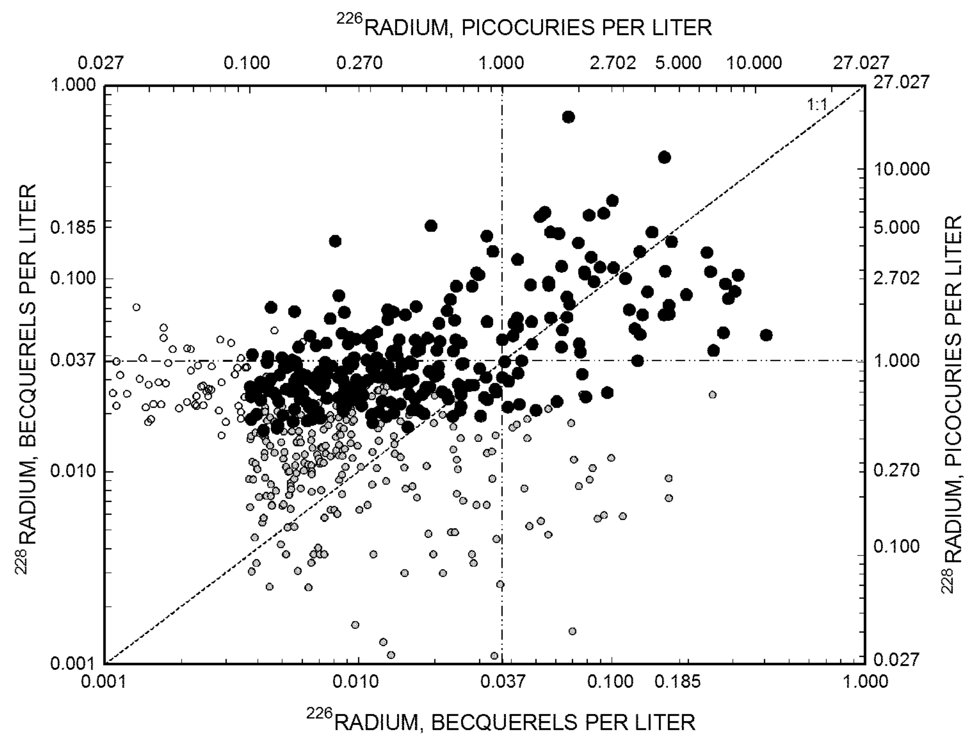

Fig. 5. Relationships between concentrations of ^{228}Ra and ^{226}Ra in water samples from 15 principal aquifer systems of the USA, 1998–2005. [Solid symbol, concentration for both isotopes greater than or equal to the sample specific minimum detectable concentration (SSMDC) data-quality performance indicator; gray symbol, concentration for the ^{226}Ra isotope greater than or equal to SSMDC; open symbol, concentration for the ^{228}Ra isotope greater than or equal to SSMDC. Dashed diagonal line is the 1:1 line. A vertical and horizontal dashed line indicates the concentration of 0.037 Bq/L or 1 pCi/L.]

CPTG. Only three lithologic types had concentrations greater than the respective SSMDCs in 33% or more of the collected samples: the quartzose coastal sands, the sandstones, and the carbonate rocks (Online Supplemental Tables S-3 and S-4). Results of previous studies have also indicated that concentrations of ^{228}Ra and ^{226}Ra typically are strongly correlated, but detection of ^{228}Ra with beta counting techniques was commonly the limiting factor for describing the relationships (Hess et al., 1985; Szabo and Zapecza, 1991; Focazio et al., 2001; Szabo et al., 2005).

The concentrations of ^{224}Ra relative to those of ^{228}Ra are reasonably described (for samples where both were greater than the respective SSMDCs) as approximately clustered about a line whose slope is nearly 1 (0.915; Fig. 6. The intercept was nearly 0 and was statistically not significant). The correlation between concentrations of ^{228}Ra and ^{224}Ra is reasonable in that both isotopes originate from the decay series of ^{232}Th. The similarity in concentrations was notable in water samples for which concentrations were greater than 0.037 Bq/L, with a median activity ratio of 1.04. The elevated concentrations of ^{224}Ra and ^{228}Ra co-occurred in PAs composed of unconsolidated, recent (late Tertiary, Quaternary, Holocene) sand. Concentrations of ^{224}Ra were commonly high (>0.037, or even 0.074 Bq/L) and those of ^{228}Ra were commonly low (<0.037 Bq/L) (Fig. 6) in a subset of about 15% of the samples that were mostly from PAs in the western USA, from the HPTA, MWAF, MWFT, PCAF, and RGBR (Figs 3 and 4). Scatter in relative terms was greatest for corresponding concentrations of ^{224}Ra and ^{228}Ra less than 0.037 Bq/L (Fig. 6), with the large relative analytical uncertainty and limited detection performance likely obscuring trends.

3.4. Relative distribution of radium radionuclide concentrations (isotope activity ratios)

The relative abundance of the three Ra isotopes was nearly equal (nearly 1:1:1 activity ratio) in samples from a limited number of PAs, such as from the CPNA PA, and the Ra isotope data from there plot near the center of the trilinear axes shown in Fig. 7. The differences between ^{224}Ra and ^{228}Ra concentrations for most samples from the CPNA PA were relatively small, even though concentrations of both isotopes were typically greater than 0.037 Bq/L, and indicate that the isotopes of Ra are readily soluble there. A slight bias towards the concentrations of ^{224}Ra and ^{228}Ra relative to those of ^{226}Ra were noted, indicating relatively minor enrichment of progeny from ^{232}Th relative to those of ^{238}U. On the other hand, a number of the samples from the PAs from the western USA plotted strongly in the ^{224}Ra dominated portion of the trilinear (distribution) diagram (Fig. 7). The aquifer matrix of fluvial, alluvial and basin-fill sands from many of these PAs are variegated, but are commonly arkosic (Michel and Cothern, 1986), are derived from granitic plutons, and are U- and Th-rich (Duval and Riggle, 1999; Table 1). In some of these PAs (MWAF, PCAF, RGBR), the concentrations of U and ^{222}Rn in the water are typically among the highest in the USA (Tables 1 and 3). Yet, among the Ra isotopes, it is only the concentrations of ^{224}Ra that were occasionally elevated in the water from these PAs (Figs. 3, 4 and 7; Table 3).

The process that explains the detection of ^{224}Ra at concentrations greater than those of ^{228}Ra in water in Th-rich (^{228}Ra-bearing) fluvial, alluvial and basin-fill sands in the western USA is recoil enrichment of ^{224}Ra relative to ^{228}Ra. The $^{224}Ra/^{228}Ra$ ratios exceed unity when the possible mechanism is combined alpha recoil of the short-lived ^{224}Ra and limited Ra solubility (mobility) controlled by adsorption onto Fe- and Mn-oxides and/or clay minerals. Alpha recoil from minerals in the aquifer matrix alone where radioactive equilibrium is established would generate a $^{224}Ra/^{228}Ra$ ratio in the groundwater that approximately mimics that of aquifer solids, which is one or very near one. The rapid and equal adsorption of the two Ra isotopes (controlled by aquifer geochemistry) combined with preferential faster recoil of ^{224}Ra generate the $^{224}Ra/^{228}Ra$ ratio >1. The mineral grains have a coating of oxides that contains an accumulation of insoluble and adsorbed isotopes of Th as the process of weathering proceeds (Tricca et al., 2001; Reynolds et al., 2003), and the direct recoil into adjacent pore space of the ^{224}Ra from the short-lived ^{228}Th parent (1.9-a half life) rich in the grain-coating oxides leads to enrichment of the ^{224}Ra in solution. Recoil damage to crystal lattice structure within the mineral grains (Fleischer, 1980) may also lead to further preferential release (desorption and diffusion from the grain interior, or indirect recoil)

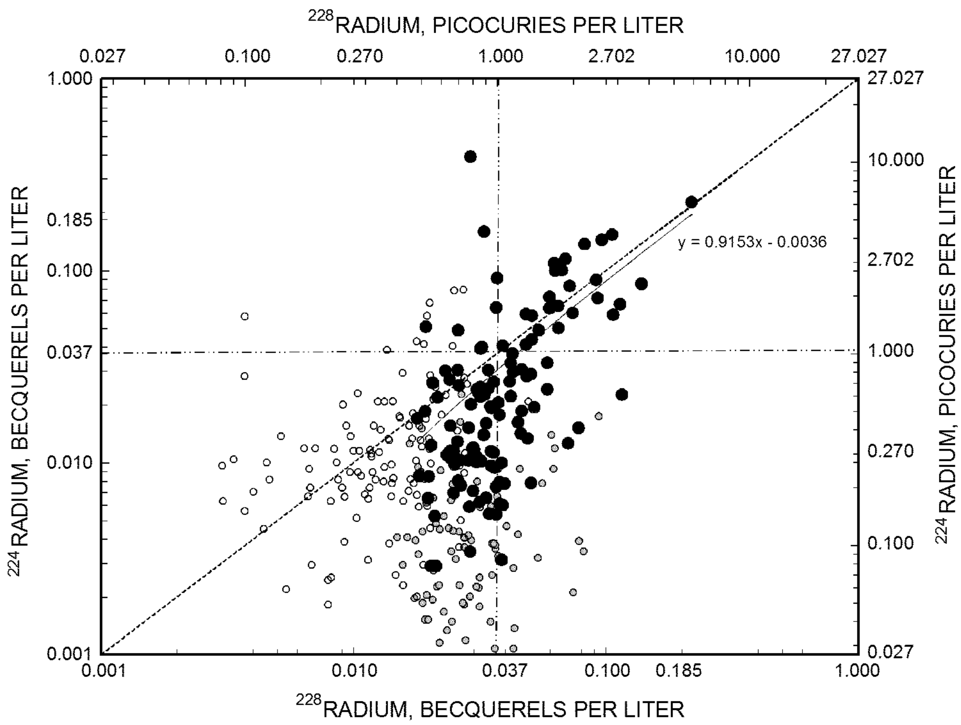

Fig. 6. Relationships between concentrations of ^{224}Ra and ^{228}Ra in water samples from 15 principal aquifer systems of the USA, 1998–2004. [Solid symbol, concentration for both isotopes greater than or equal to the sample specific minimum detectable concentration (SSMDC) data-quality performance indicator; gray symbol, concentration for the ^{228}Ra isotope greater than or equal to SSMDC; open symbol, concentration for the ^{224}Ra isotope greater than or equal to SSMDC. Dashed diagonal line is the 1:1 line. The best fit line (solid) shown had a slope of 0.915 for the ^{224}Ra and ^{228}Ra isotope pair. A vertical and horizontal dashed line indicates the concentration of0.037 Bq/L or 1 pCi/L.]

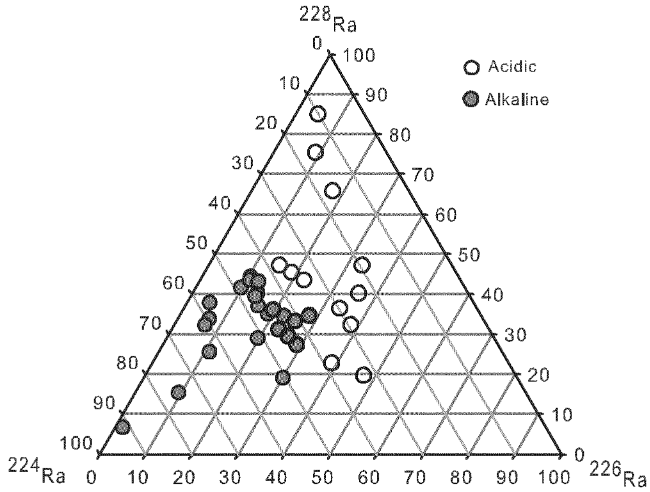

Fig. 7. Ternary diagram showing relative concentrations of Ra isotopes (^{224}Ra, ^{226}Ra, and ^{228}Ra) in samples in which all 3 were present at detected concentrations in the acidic quartzose Coastal Plain, North Atlantic principal aquifer system (open circles) and the alkaline basin-fill and alluvial sands of the High Plains Tertiary alluvium, Mountain West alluvium and fill, Pacific Coastal alluvium and fill, and Mountain West Foreland Basins Tertiary sandstone principal aquifer systems (solid circles), 1998–2004. [Principal aquifer descriptions are provided in Table 1 and locations are shown in Fig. 1.]

of the progeny forming in latter parts of the decay series, such as the ^{224}Ra isotope that is many decays removed from the original ^{232}Th parent. Any change in aquifer geochemistry affecting Ra mobility, whether along a flowpath or temporal, can further enhance high values of the ratio because ^{224}Ra will reach steady state concentrations faster than longer-lived ^{228}Ra (Sturchio et al., 1993). Where Ra solubility is low, the excess contribution of ^{224}Ra released to solution by the (physical) recoil mechanism relative to the overall amount of ^{228}Ra released by leaching could be substantial. The excess contribution of ^{234}U released to solution relative to the parent isotope, ^{238}U, by the (physical) recoil mechanism can be substantial where U is of low solubility (Osmond and Cowart, 1976; Gilkeson and Cowart, 1987), but the processes are not identical because U isotopes have longer half lives than do the isotope pair of ^{224}Ra and ^{228}Ra, and the U isotope ratios may vary in source rock and soil.

Where Ra is reasonably soluble, on the other hand, the excess contribution of ^{224}Ra mobilized to solution by the physical recoil process relative to dissolution (leaching by chemical weathering) of ^{228}Ra is relatively small. Isotopic ratios for the ^{224}Ra/^{228}Ra near 1 are expected when large values of both (usually >0.037 Bq/L) are present and represent a condition where Ra isotopes are somewhat soluble (adsorptive distribution coefficient is relatively small). Relatively large concentrations of both isotopes (often near 0.185 Bq/L) are noted in the waters from the CPNA PA (Fig. 3). The waters in the CPNA are noted to be among the most acidic among all the PAs (median and minimum pH, 5.6 and 4.0, respectively) and thereby are in strong contrast with the alkaline chemistry of the PAs from the western USA (median pH range is from 7.2 to 7.9 for water samples from the HPTA, MWAF, MWFT, PCAF, and RGBR PAs, with a maximum of 9.3; Table 1). The solubility of Ra in waters and the isotopic ratios (especially for ^{224}Ra/^{228}Ra) are thus partly related to the varying geochemical conditions.

The ^{228}Ra/^{226}Ra activity ratios for the water samples can be affected by the ratio of concentrations of the long-lived parents, Th and U, respectively, in the aquifer matrix. The water from unconsolidated to semi-consolidated sands all typically had ^{228}Ra present in higher concentrations than ^{226}Ra, whether they were quartzose coastal sands (CPNA PA), or whether they were arkosic or lithic-fragment-rich fluvial, alluvial and valley-fill sands (RGBR, PCAF, HPTA, and WMAF PAs). The median ^{228}Ra/^{226}Ra activity ratios for the water samples from the CPNA PA of 1.32 was the lowest median ratio among these PAs with sand matrix; among the remaining 4 PAs, the median ^{228}Ra/^{226}Ra activity ratios were 2.85, 3.51, 3.91 and 4.97, respectively (Online Supplemental Table S-4). For 3 of these PAs (PCAF, WMAF and RGBR), in all the samples where concentrations of both Ra isotopes were greater than the SSMDCs, ^{228}Ra concentrations were greater than corresponding concentrations of ^{226}Ra.

Enrichment of ^{226}Ra relative to ^{228}Ra (note it is the ^{226}Ra/^{228}Ra greater than 1.0 in this case) was noted in waters especially from the carbonate-rock-type aquifer systems, and is a plausible product of the enrichment of U (relative to Th) in carbonate minerals (Sturchio et al., 2001). For the water samples from the MCOO PA, the median ratio of ^{226}Ra/^{228}Ra was 1.84, the maximum ratio was 5.98, and the ratio of ^{226}Ra/^{228}Ra in more than 75% of the water samples was greater than 1. Similarly, the ratio of ^{226}Ra/^{228}Ra in 89% of the water samples collected by Sturchio et al. (2001) from Midcontinent carbonate aquifers was greater than 1.5. The median ^{226}Ra/^{228}Ra ratio was about 1.0 for water samples in this study from the phosphatic limestones of the FLRD, but large ^{226}Ra/^{228}Ra ratios were measured (maximum, 3.76). The high solubility of ^{238}U (Langmuir, 1978) relative to ^{232}Th (insoluble; Langmuir and Herman, 1980) is the cause for the widespread distribution, redistribution and enrichment of U relative to background levels in marine carbonate deposits and siliclastic sediment deposits that undergo diagenetic reactions to form sandstone. Uranium can form complexes with organic-matter residues and become enriched relative to background in organic C-rich sands, sandstones, and shales (Swanson, 1962; Turner-Peterson, 1985). The lithified sandstones composing the APMB PA fit this description, for example (Turner-Peterson, 1980), as do perhaps some unconsolidated, semi-consolidated, and consolidated closed basin sediment deposits from the RGBR PA (Turner-Peterson, 1985; Thomas et al., 1993). The concentration of ^{226}Ra was on occasions enriched relative to that of ^{228}Ra in a subset of samples of water from the APMB PA, with maximum ^{226}Ra/^{228}Ra activity ratio of 3.0. Locally variable U enrichment relative to Th is likely.

The ^{228}Ra/^{226}Ra isotope activity ratio data for ground water of the USA show ratios that typically are enriched in ^{228}Ra relative to ^{226}Ra in the clastic sand aquifers, and the ratios were comparable to the activity ratio data for these Ra isotopes compiled worldwide from sand and sandstone aquifers by Vengosh et al. (2009); they obtained a median ^{228}Ra/^{226}Ra isotope activity ratio of 1.6, with ratios from individual samples exceeding 5, and median ratios from a major sandstone aquifer studied of about 2.9. The ^{228}Ra/^{226}Ra isotope activity ratio results from the sand aquifer systems in this study were also consistent with slight enrichment of ^{228}Ra relative to ^{226}Ra from major estuaries and rivers that drain major parts of the North American continent, including the Atchafalaya, Delaware, Mississippi and Pee Dee Rivers (Elsinger et al., 1982; Elsinger and Moore, 1983; Krest et al., 1999). The exception is the lower Mississippi River (Kraemer and Curwick, 1991) perhaps because of industrial input from phosphatic limestone. The ^{228}Ra/^{226}Ra isotope activity ratios in streams traversing the Indian subcontinent (Sarin et al., 1990) indicate a pattern similar to that for ground and stream waters of the USA, with dominance of ^{228}Ra relative to ^{226}Ra in sand and sandstone terranes, and conversely, dominance of ^{226}Ra relative to ^{228}Ra in carbonate-rock terranes.

3.5. Relationships among radium, uranium, and gross alpha-particle activity

The gross alpha-particle activities measured by the conventional technique (no specified holding time) corresponded and correlated more strongly with the concentration of U than with that of

^{226}Ra (Table 4; Online Supplemental Tables S-6 and S-7). This result is explained by the widespread occurrence of oxic and neutral to alkaline ground water used for drinking water in the USA (Table 1) in which U is strongly soluble (Hodge et al., 1998; DeSimone, 2009; Jurgens et al., 2009). The U frequently occurs at concentrations that contribute considerable gross alpha-particle activity to the water. There is correspondence between gross alpha-particle activity and high concentrations of ^{226}Ra, but only in a smaller subset of samples than is the case for U (Table 4). The conventional compliance monitoring for gross alpha-particle activity as an indicator for where combined Ra exceeds the MCL as suggested by Hess et al. (1985) may be an inadequate screening test for Ra occurrence except perhaps for the few PAs where U is absent from the water. An adequate application of such a screening scenario might best fit the CPNA PA, where Ra radionuclide concentrations are among the highest and U concentrations are among the lowest among the PAs (Table 3).

The common presence of ^{224}Ra in moderate to high concentrations in waters from the coastal sand aquifer systems of the eastern USA and the occasional presence of ^{224}Ra in high concentrations in waters from the western USA was documented in this study (Fig. 4), with the maximum ^{224}Ra concentration of 0.392 Bq/L (10.6 pCi/L) determined from alluvium in the MWAF PA (Fig. 3). This particular ^{224}Ra-rich sample did not have a corresponding measurement of gross alpha-particle activity within 72 h after sample collection, however, and the effect of the ^{224}Ra could thus not be determined. The effect of ^{224}Ra concentration on gross alpha-particle activity within 72 h and 30 days after sample collection was considered for 134 samples from the western USA; gross alpha-particle activities declined by a difference that exceeded the precision estimate (pe) in 9 (6.7%) of the samples, with the magnitude of the difference in each greater than 0.074 Bq/L (2.0 pCi/L). All nine of those samples had detectable concentrations of ^{224}Ra, most with concentrations from 0.037 to 0.074 Bq/L, with a maximum of 0.109 Bq/L (2.95 pCi/L). The high initial gross alpha-particle activity within 72 h of sample collection and decline with time resulting from the decay of ^{224}Ra could be observed even in the samples in which U isotopes were predominant (with concentrations exceeding 10 μg/L). The moderate to low frequency for substantial gross alpha-particle activity decline observed in ground waters from the western USA in this study was consistent with the moderate to low frequency of elevated ^{224}Ra concentrations observed. Ruberu et al. (2005) in a survey of ground water from California similarly observed only the occasional presence of ^{224}Ra in moderate to high concentrations. The occasional ^{224}Ra occurrence can affect gross alpha-particle activity in the western USA, however.

4. Discussion

4.1. Importance of geochemistry for occurrence of the higher concentrations of radium in the principal aquifer systems

Concentrations of Ra were found to significantly relate to select geochemical environments and the major overall geochemical characteristics of the ground waters, such as pH, DO and total dissolved solids. The geochemical characteristics varied widely among the PAs, and the variables pH, DO, and total dissolved solids (represented here by the frequently measured surrogate, specific conductance, SC) were broadly representative of the major aspects of ground-water geochemistry (acidity, oxidation–reduction potential, and the amount of mineralization, respectively) by which the geochemical environments (providing controls) of Ra occurrence can be broadly classified. (See Table 1 and Online Supplemental Information for details.) The critical relationships between Ra occurrence and geochemical characteristics of the waters can be understood in the context that the PAs where Ra concentrations in water were highest had among the lowest U and Th contents in the aquifer solids (Table 1), and the conventional measurements of the general amount of radioactivity in the water, such as measurements of gross alpha-particle activity, or the concentrations of ^{222}Rn or U, provided no reliable means for identifying where combined Ra concentrations were routinely elevated (Tables 3 and 4).

4.2. Relationships between concentrations of radium, dissolved oxygen and pH

Concentrations of combined Ra were statistically significantly different among broad groups when waters were classified on the basis of the pH and the DO content, with the highest concentrations among the near neutral to alkaline and anoxic (pH > 6, DO < 1 mg/L), acidic and oxidizing (pH < 6, DO > 1 mg/L), and acidic and anoxic (pH < 6, DO < 1 mg/L) water-chemistry groups (Table 3). The frequency of occurrence of combined Ra in concentrations greater than the MCL was highest (9.7%) among the acidic oxidizing water samples, and concentrations greater than the MCL and 0.037 Bq/L were found to be most common within these three water-chemistry groups. Of the 40 samples in which the com-

Table 4
Number of detections within ranges of gross alpha-particle activities with U and ^{226}Ra concentrations for 757 water samples from 15 principal aquifer systems in the USA, 1998–2004. Italics indicate low constituent concentrations that cannot account for the gross alpha-particle activity [1 Bq/L = 27.027 pCi/L; MCL, maximum contaminant level; ND, non detect].

Uranium concentration in μg/L		Gross Alpha activities in Bq/L [pCi/L]		
		<0.370 [<10]	0.370–0.555 [10–15]	≥0.555 (MCL) [≥15 (MCL)]
≥30 (MCL)		9	1	17
20–29.99		6	7	7
10–19.99		20	5	6
<10, but detected		411	7	14
NDffi<10		218	3	5
Totals		664	23	49
^{226}Radium concentration in				
Bq/L	pCi/L			
≥0.185 (MCL)	≥5 (MCL)	–	–	4
0.111–0.185	3–4.99	2	–	1
0.037–0.111	1.0–2.99	30	3	7
0.004–0.037	0.11–0.99	312	18	24
NDffi<.004	NDffi<0.11	334	5	17
Totals		678	26	53

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bined-Ra concentration (or in one case, ^{226}Ra concentration alone) exceeded the MCL, waters with either low DO concentration and near-neutral to alkaline conditions (25 of 40, or 62.5%), with low pH and oxic conditions (12 of 40, or 30.0%), or low DO concentration in combination with low pH (2 of 40, or 5.0%) accounted for 39 samples (97.5%) (Online Supplemental Fig. S-2). The one remaining sample with combined Ra concentration greater than the MCL was characterized by "mixed" redox conditions indicating anoxic water was entering the well bore at some productive interval. In similar fashion, concentrations of combined Ra were highly likely to exceed 0.037 Bq/L in waters with low DO concentration (26.6%), low pH (37.2%), or low DO concentration in combination with low pH (50.0%). The near-neutral, neutral and alkaline waters, when oxic, had a low frequency of occurrence of concentrations of combined Ra > 0.037 Bq/L of 14.3% and the MCL of 0.3% (Table 3). The three water-chemistry groups defined by low pH, low DO concentration, or by the combination of the two were found to occur with moderate to high frequency in all of the PAs where the elevated Ra concentrations were present.

The effect of enhanced mobility of Ra in the anoxic type waters is among the most important factors explaining the occurrence of elevated concentrations of Ra in the USA because of the frequent occurrence of anoxic and near-neutral to alkaline type ground water in broad regions of the northeastern, southeastern, and central USA. Of the 15 PAs studied, 6 PAs (CNEY, CPTG, FLRD, GLCL, MCOO, and the MWTF) had the common occurrence of anoxic water, with median DO < 1.1 mg/L for each (Table 1). All the PAs with low DO concentrations were classified by the Tukey–Kramer test as belonging to one of the two higher Ra-concentration groups among the PAs (Table 3). The frequency of occurrence of concentrations of combined Ra > 0.037 Bq/L among samples of water with DO concentration < 1 mg/L from these 6 PAs about equals or mostly exceeds the overall frequency of occurrence in oxic near-neutral, neutral and alkaline waters of 14.3% and the overall national frequency of occurrence of 26.8% except for 1 PA (GLCL) (Online Supplemental Tables S-3). Water samples from the APMB PA were less frequently anoxic than from those other 6 PAs, but combined Ra concentration > the MCL and P 0.037 Bq/L were associated with anoxic samples. The frequency of occurrence of concentrations of combined Ra > 0.037 Bq/L (or in a few cases, of the one measured isotope of Ra with concentration > 0.037 Bq/L) among samples of water with DO concentration < 1 mg/L from these 7 PAs are as follows: the MCOO, 37 of 47 samples (78.7%), APMB, 4 of 6 samples (66.7%), FLRD, 26 of 64 samples (40.6%), CPTG, 17 of 51 samples (33.3%), MWTF, 7 of 24 samples (29.2%), CNEY, 12 of 47 samples (25.5%), and GLCL, 28 of 201 samples (13.9%; but with slightly greater frequency of occurrence in New England of 16.7%). Among the PAs such as the APVR, PCAF, and RGBR, the limited numbers of combined Ra concentrations > 0.037 Bq/L were also found with greater frequency in anoxic waters (DO concentration < 1 mg/L) than in those that were oxic.

Concentrations of combined Ra with respect to DO in a subset of 4 (MCOO, APMB, CNEY, and GLCL of the northeast) of the PAs for which at least one sample contained combined Ra at a concentration > MCL are shown in Fig. 8. The relationship of combined Ra with DO is near hyperbolic indicating that Ra concentrations are most elevated when DO is absent, and conversely Ra is low or absent when DO is abundant. (The hyperbolic relationship is equally evident when the concentrations of ^{226}Ra, the isotope that represents the large bulk of the mass of the Ra in solution, are shown as a function of DO in Online Supplemental Fig. S-3.) Statistically significant negative correlation of concentrations of combined Ra with those of DO was noted among the samples from the APMB, FLRD, and GLCL PAs (Online Supplemental Table S-5).

Concentrations of combined Ra in excess of 0.037 Bq/L and 0.185 Bq/L were found in acidic water samples (pH was less than 6.0) at a frequency of 37.2% and 9.7%, respectively, which is proportionately a greater frequency than in other water types (Table 3). The occurrences of acidic waters were not as widespread as that of anoxic waters, however, and were found especially in PAs in the northeastern, eastern and southeastern USA, especially in those consisting of unconsolidated coastal quartzose sand (Table 1). Elevated concentrations of combined Ra and all 3 individual Ra isotopes are routinely highest in waters with pH < 6 in the CPNA, CPSE, and GLCL (in New England) PAs, with the increase in combined Ra concentrations becoming most notable among the samples for which pH was below 5.5 (Fig. 9; see also Online Supplemental Fig. S-4 for the similar trend for the ^{226}Ra isotope). The frequency of occurrence of concentrations of combined Ra > 0.037 Bq/L is greatest for the samples with the lowest pH, including 22 of 24 samples (91.7%) with pH < 5.0 in the CPNA and in 5 of 6 samples (83.3%) with pH < 5.5 in the GLCL (in New England). The MCL was mostly exceeded in those cases with the most acidic waters. The maximum combined-Ra concentration 0.755 Bq/L (20.4 pCi/L) was associated with strongly acidic water (pH 4.4) in the CPNA (Fig. 9). Statistically significant negative correlation of concentrations of combined Ra with pH was noted for the entire data set and among the samples from the CPNA and CPTG PAs (Online Supplemental Table S-5). Concentrations of combined Ra, ^{228}Ra, and ^{226}Ra show a strong inverse relationship with pH in the acidic oxidizing waters (Online Supplemental Table S-6).

4.3. Relationships among ground-water chemistry, lithology, and radium occurrence

Concentrations of combined Ra were substantially loaded to each of the first three principal components (PCs) for the entire data set defined by principal components analysis (PCA), the range of the absolute values of the loading (r) of combined Ra was 0.128–0.226. These three PCs given in Table 5 represented readily recognizable major components of ground-water geochemistry that related to mineralization (component 1, PC1), oxidation–reduction and DO (component 2, PC2), and acidity (component 3, PC3), respectively. (Listed in Table 5 for the overall data set and also for each PA are the component numbers for which Ra loading was noted, the fraction of variance they explain, and the value of the eigenvector. Loadings of additional constituents are shown as Online Supplemental Tables S-8 and S-9.) Mineralized waters were indicated by positive loadings on PC1 of the values of SC (loading, 0.356), and of the concentrations of Ca, Mg, K, Na, SO_4 and alkalinity (all loadings from 0.272 to 0.316), and to a lesser extent, those of Cl and Ra (loading, 0.128), generally indicating the effects of bedrock weathering. The constituents that loaded on PC2 had concentrations most affected by oxidation or reduction. Strong inverse loading with the concentrations of Fe, Mn and Ra (ffi0.467, ffi0.465, and ffi0.226, respectively) indicated the preferential occurrence of these three constituents in anoxic environments. Oxic environments were indicated by direct loading on PC2 of the concentrations of DO (0.380) and to a lesser extent NO_3. Acidic waters were indicated by inverse loading on PC3 of the pH (ffi0.497) and the concentrations of alkalinity (ffi0.360) with direct loadings of the concentrations of Ra (0.195), Al (0.301), and NO_3 (0.282). The largest of the loading values with respect to combined Ra concentration is the corresponding (direct) relationship with Mn and Fe illustrated by PC2 indicating the strong association of combined Ra with anoxic waters (also reflected by the opposing (inverse) relationship with DO and NO_3). The component PC2 is thus listed most prominently (first) in Table 5. The next largest of these loading values with respect to combined Ra concentration is the inverse relationship with pH (PC3) and is listed second in Table 5.

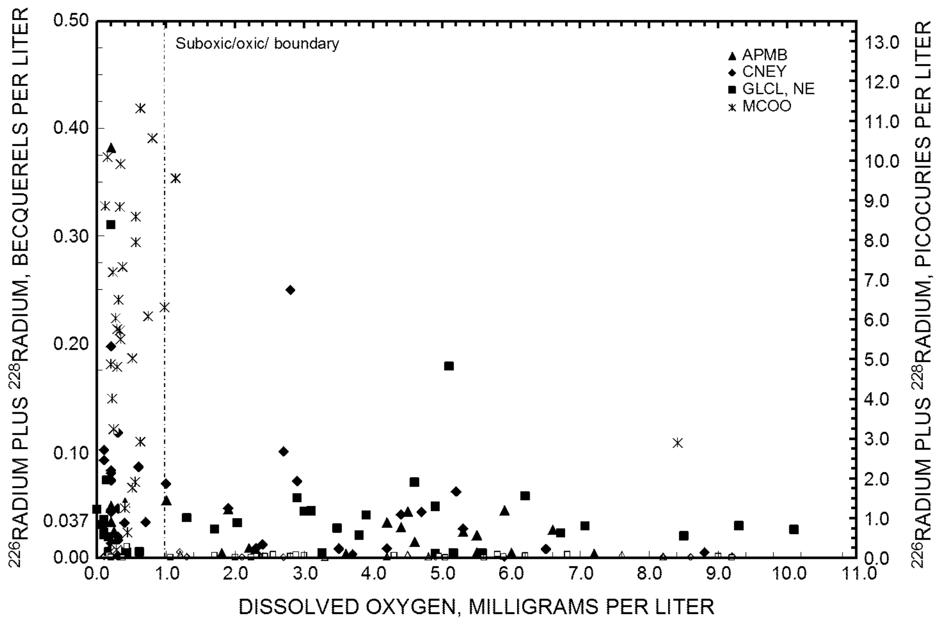

Fig. 8. Relationship of concentrations of ^{226}Ra plus ^{228}Ra and dissolved O_2 for samples from selected principal aquifer systems of the USA, 1999–2005, the Appalachian Piedmont Mesozoic Basins (APMB), the crystalline (granite, metamorphic) rocks of New England (CNEY), the glacial sand and gravel from New England (GLCL NE), and the Mid-continent and Ozark Plateau Cambro-Ordovician dolomites (MCOO). [Solid symbol, concentration for one or both isotopes greater than or equal to the sample specific minimum detectable concentration (SSMDC) performance indicator; open symbol, concentration for both ^{226}Ra and ^{228}Ra isotopes were less than the SSMDC. All samples contained at least one Ra isotope concentration greater than the respective SSMDC for the MCOO principal aquifer. Relationship of concentrations of ^{226}Ra and dissolved O_2 for samples from the same selected principal aquifer systems, 1993–2005, is shown in Online Supplemental Fig. S-3.]

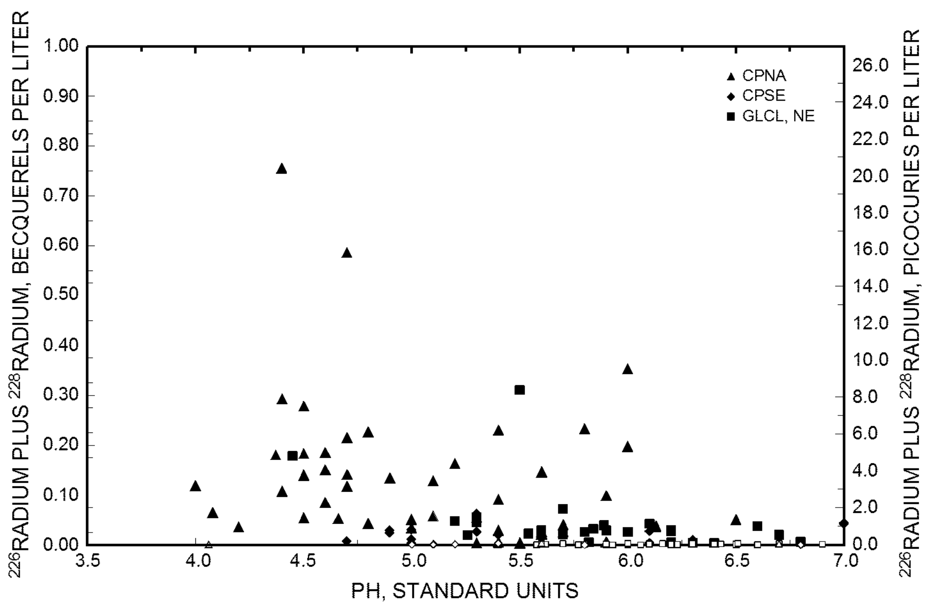

Fig. 9. Relationship of concentrations of ^{226}Ra plus ^{228}Ra with pH for samples from selected acidic principal aquifer systems of the USA, 1998–2004, the Coastal Plain, North Atlantic (CPNA), the glacial sand and gravel from New England (GLCL NE), and the Coastal Plain, southeastern (CPSE). [Solid symbol, concentration for one or both isotopes greater than or equal to the sample specific minimum detectable concentration (SSMDC) performance indicator; open symbol, concentration for both ^{226}Ra and ^{228}Ra isotopes were less than the SSMDC. Relationship of concentrations of ^{226}Ra with pH for samples from the same selected acidic principal aquifer systems, 1998–2004, is shown in Online Supplemental Fig. S-4.]

Though not particularly strong, the positive loading for combined Ra with PC1 including with SC and with most major dissolved constituents, especially with concentrations of Ca and Mg, does provide evidence for a "competing ion" effect on Ra occurrence in mineralized waters. The SC was moderately correlated with concentrations of all the Ra isotopes (r, +0.295 for ^{226}Ra; Online Supplemental Table S-6) but correlations were somewhat stronger for divalent cations, Ca, Mg, Ba and Sr (range for r, +0.315–0.385 for ^{226}Ra). Among the anoxic Ra-rich waters, the SC of some were about 1000–3000 lS/cm, that is, moderately mineralized. At the moderate to low salinities of ground water used for drinking water, Vengosh et al. (2009) did not note a globally consistent correlation with generally increasing concentrations of Ra and increasing "mineralization". It is in more brackish to saline water that this

Table 5
First three principal component (PC) loadings for all water samples from 15 principal aquifer systems (PAs) of the United States collected 1998–2005 for concentrations of ^{226}Ra plus ^{228}Ra (combined Ra) on the basis of 22 selected constituents. Also, PC loadings for each principal aquifer for which concentrations of combined Ra constitute a major component (loading, r, typically greater than [0.20]) and which explains greater than 5% of the variability of the water-quality. [PCN, Principal Component Number. General geochemical group for Ra occurrence from principal components on the basis of correlated constituents: Anoxic, direct with Fe and Mn and indirect with dissolved O_2 (DO) and NO_3 (light shading), Acidic, direct with Al and NO_3 and indirect with pH, alkalinity, and silica (dark shading); Mineralized, direct with specific conductance (SC), Ca, alkalinity, SO_4, K and other major constituents. Bold, loadings of combined Ra and loadings greater than [0.20]; italic, loadings less than [0.10]. Loadings for As, U and Se rarely were substantial for those components for which Ra demonstrated substantial loading and loadings for Co were nearly identical to those of Ni; loadings for a larger subset of these constituents are shown in the Online Supplemental Information. PAs in bold type are those with at least one combined-Ra concentration greater than or equal to the Maximum Contaminant Level (0.185 becquerels per liter, or 5 picocuries per liter). Excluded from PC analysis were gross measures of radioactivity (gross alpha and beta-particle activity and ^{222}Rn concentration) and the majority of trace elements. Light shading, constituents associated with anoxic conditions; darker shading, constituents associated with acidic conditions.]

General geochemical group for Ra occurrence for Principal Aquifer Systems (from principal components for each aquifer system)[1]																
	Anoxic[2]	**Acidic**[2]	**Mineralized**[2]	**Anoxic**	**Anoxic and Mineralized**									**Acidic and Anoxic**		**Acidic**
	Entire Data Set			Carbonate rocks		Mixed[3]	Sandstones			Crystalline[4]	Alluvial[5]	Glacial		Coastal Plain sands		
Constituent	**ALL**	**ALL**	**ALL**	**FLRD**	**MCOO**	APVR	**APMB**	MWFT[6]	MWFT[6]	**CNEY**	HPTA	**GLCL**	**CPTG**	CPSE	CPSE	**CPNA**
$^{226}Ra + ^{228}Ra$	**-0.226**	**0.195**	**0.128**	**0.222**	**0.175**	**0.159**	**0.218**	**0.296**	**0.279**	**0.258**	**0.159**	**0.161**	**0.164**	**0.343**	**-0.208**	**0.268**
DO	**0.380**	**0.205**	-0.144	*-0.052*	-0.108	**-0.262**	**-0.319**	0.125	**-0.231**	**-0.210**	-0.191	**-0.242**	-0.180	*-0.056*	**0.360**	**0.278**
Iron	**-0.467**	*-0.054*	0.106	0.150	**0.231**	0.175	**0.287**	*0.055*	*-0.029*	0.175	0.177	**0.209**	*0.086*	0.177	*0.028*	-0.195
Manganese	**-0.465**	*0.070*	0.100	**0.274**	**0.218**	*0.097*	**0.258**	0.192	**0.214**	0.156	**0.237**	0.196	0.166	*0.097*	**0.209**	*-0.019*
Nitrate	**0.432**	**0.282**	*0.018*	*0.049*	*-0.081*	*-0.052*	**-0.295**	**0.237**	-0.192	*0.012*	-0.109	*-0.096*	*-0.084*	*-0.052*	**0.369**	**0.353**
pH	*0.066*	**-0.497**	0.119	**-0.283**	-0.150	**0.295**	0.192	**-0.328**	*0.055*	*0.069*	*-0.072*	*0.014*	**0.247**	**-0.261**	**-0.252**	**-0.207**
Alkalinity	*0.051*	**-0.360**	**0.285**	0.132	*0.059*	**0.293**	**0.336**	*-0.085*	*-0.070*	0.139	**0.217**	**0.291**	**0.369**	-0.134	-0.122	-0.147
SC	*0.016*	*-0.085*	**0.356**	*0.059*	**0.308**	**0.350**	**0.309**	0.154	*-0.033*	**0.402**	0.142	**0.384**	**0.411**	-0.196	*0.025*	0.116
Calcium	*0.080*	*-0.061*	**0.316**	**0.385**	**0.284**	**0.314**	**0.273**	**0.338**	*-0.089*	**0.291**	**0.232**	**0.324**	**0.267**	*-0.056*	**0.254**	0.133
Magnesium	*0.093*	*-0.029*	**0.314**	0.100	**0.284**	**0.297**	**0.265**	**0.320**	-0.188	**0.298**	**0.264**	**0.344**	**0.266**	*0.063*	**0.374**	0.160
Sulfate	*0.055*	*0.046*	**0.301**	**0.232**	**0.308**	**0.257**	0.191	0.188	*-0.094*	0.163	**0.291**	**0.234**	0.109	0.171	*0.044*	**0.283**
Barium	*-0.034*	*0.058*	0.171	0.110	**-0.252**	**0.223**	-0.160	*0.018*	**0.331**	**0.272**	-0.151	**0.315**	**0.251**	0.163	**0.367**	**0.245**
Fraction of variance[7]	0.136	0.114	0.270	0.239	0.425	0.299	0.259	0.333	0.082	0.208	0.369	0.259	0.218	0.137	0.071	0.204
PCN	2	3	1	1	1	1	1	1	4	1	1	1	2	2	4	2
Eigen vector	2.991	2.509	5.937	5.252	9.357	6.578	5.704	7.327	1.802	4.584	8.121	5.704	4.801	2.606	1.342	4.494

[a] Low Ra occurrence and no readily interpretable geochemical relations on the basis of PCA for MWAF, PCAF, RGBR, and BSLT PAs.
[b] PCs shown in order of significance with respect to Ra occurrence, not significance with respect to explaining variance for the entire data set.
[c] Intermixed Sandstones and Carbonate Rocks.
[d] Crystalline (Felsic to Intermediate) Igneous and Metamorphic Rock.
[e] Alluvial, or Fluvial sands and gravels.
[f] Strong loading for combined Ra with PC1 for MWFT PA but the combination of loadings does not readily fit as representative of anoxic, acidic, or mineralized type waters.
[g] Fraction of variance explained by the particular PC.

correlation holds more consistently (Kraemer and Reid, 1984; Sturchio et al., 2001).

The most statistically significant component to which the concentrations of combined Ra loaded significantly (typical values of r, P [0.20–0.40]) for each PA is given in Table 5 and illustrates the commonality of relationships among ground-water chemistry, and Ra occurrence among the various PAs. The most common factors relating to Ra occurrence individually or in combination, as indicated by the PC that explains the most variance and that also has substantial loading for Ra, are PCs comprised of groupings of constituents relating to the occurrence of anoxic (low DO) waters, with high loadings for the concentrations of Fe and Mn, and with groupings of constituents associated with a moderate degree of mineralization. These relationships cross-cut nearly all lithological types in the PAs. The constituents whose strong loadings related to anoxic waters are displayed at the top in Table 5 and are shaded in light gray. The loading of Ra and constituents commonly associated with anoxic waters onto a single PC was a prominent descriptor of the (variance of the) geochemistry of most of the PAs (as many as 10 of the 15 studied). Concentrations of combined Ra loaded strongly with constituents describing acidic conditions for 2 PAs (quartzose coastal sand aquifer systems). The constituents that represent association with acidic waters are shaded in dark gray in the middle rows of Table 5. The loading for Ca, Mg and Ba, and the corresponding loading of combined Ra was common for most of the PAs; this set of relationships for the PCs is most consistent with the presumed effect of competing ions on increased Ra occurrence.

Concentrations of combined Ra showed loadings directly with those of Fe and Mn, Ca, and SC, and indirectly with DO for the primary component for the APMB, GLCL, CNEY, MCOO, HPTA and APVR PAs. The Ra concentration was loaded onto principal components in the CPTG and MWFT PAs that also included constituents that related to anoxic and mineralized waters, but the components (second and fourth, respectively) were not primary. Radium concentration was directly loaded with concentrations of Fe and Mn in the FLRD PA (Table 5), indicative of Ra occurrence with the "anoxic fraction" of the water. Some to many samples in the CPTG, FLRD and MWFT PAs had the concurrent presence of DO, Mn, and/or Fe – mixed redox indicators, reflective of borehole mixing of water of different types (McMahon and Chapelle, 2008). All but 1 of the 13 highest combined-Ra concentrations (>0.074 Bq/L) in the FLRD PA and all but 5 of the 13 highest concentrations in the CPTG PA were associated with waters with concentration of DO < 1 mg/L, though Ra was also detected in waters of mixed redox category. The mixing of dilute oxic and anoxic/suboxic waters in individual boreholes is common in production wells with high yields in the FLRD PA (Katz et al., 2007). The loading with (and corresponding correlations with) concentrations of Ca and the SC indicate that the competing ion factor likely also has an effect on Ra occurrence in the CPTG and the MWFT PAs.

The association of acidic water type with Ra occurrence was predominant in the eastern coastal USA in the CPNA and CPSE PAs. The components describing the association were not the predominant component in either PA, but were of importance (explained the second greatest amount of variance for each PA). Acidic waters with elevated Ra concentrations were also found in the GLCL PA in New England, though anoxic waters were more common in this PA overall, and the occurrence of Ra was also associated with constituents found in anoxic and acidic waters there. The acidic water associated with elevated Ra occurrence was commonly NO_3 dominated, especially in the CPNA PA (Table 5), and to a lesser extent in the GLCL PA in New England. Septic-tank effluents and agricultural soil amendments are important NO_3 sources there (Szabo et al., 1997; Starns and Brown, 2007), and the nitrification of the septic-tank effluents and soil amendments has been shown to decrease pH in quartzose sands (Robertson et al., 1998; Szabo et al., 2010). In the NO_3-dominated waters, primarily from the areas of quartzose sediment, concentrations of all isotopes of Ra correlated strongly and inversely with concentrations of carbonate alkalinity, Ca and silica, and with pH (Online Supplemental Table S-7).

It is not coincident that geochemical environment, more so than general lithology or bedrock radioactivity, best describes the occurrence of Ra, that is, most frequent in anoxic or acidic waters in PAs in the USA. Environmental conditions must be such that the tendency of Ra toward adsorption, especially onto Fe- and Mn-oxides and oxyhydroxides, is overcome. In anoxic geochemical environment where DO is consumed and the waters are Fe- and Mn-reducing, the Fe- and Mn-oxyhydroxide coatings are thermodynamically unstable and are absent, or have little abundance; or, if some are present, they, along with clay minerals, are coated with reduced divalent Fe and Mn cations that are strongly adsorbed (Roden and Zachara, 1996; Silvester et al., 2005). The few remaining adsorption sites quickly become saturated and the sorption of other divalent cations is prevented. The sorptive properties of the aquifer material may be less than what might be possible in an oxic environment where Fe- and Mn-oxyhydroxides are abundant (reductive degradation of sorption capacity). The competing ions likely also have a notable effect on Ra occurrence especially in anoxic environments if the sorptive capacity is somewhat diminished. The additional major factor limiting Ra adsorption in the PAs is the pH of the ground water; the variable surface charge of the aquifer matrix is controlled mostly by a mixture of Fe, Mn and Al oxyhydroxides (point of zero charges about pH 7, 6 and 5, respectively; Stumm and Morgan, 1981), and as the pH approaches these values, Ra is less likely to be adsorbed. The H^+ cation itself, present at relatively high concentrations in acidic waters, competes effectively with divalent cations for sorption sites, including with Ca and Mg (Appelo, 1994), and by analogy, with Ra. Concentrations of Mn correlated with those of all three Ra isotopes and those of Fe with two, ^{224}Ra and ^{226}Ra, respectively, in acidic and oxic waters (range of r, +0.196–0.337; Online Supplemental Table S-6), Ra mobility likely corresponds with the instability of the surfaces of the oxides.

4.4. Compositional variability and affects on radium concentration for the more mineralized waters

Compositional variability among the aquifer materials and of recharge, and the variability in water residence time has substantial effects on the actual water composition, pH, and the amount of DO consumed, and thus the amount of Mn, Fe or Ra liberated to solution. The radionuclides of U, Th and Ra, and similarly, the chemical constituents, Fe, Mn, S and organic C may differ in their distribution in the solid matrix, thereby strongly affecting patterns of weathering, the initiation of redox reactions such as Mn, Fe and SO_4 reduction, and the formation and distribution of secondary minerals critical to Ra sorption and also recoil. Water from a limestone aquifer may have lower concentrations of Fe or Mn than water from a glacial sand and gravel aquifer under similar Fe-reducing conditions. Concentrations of Fe in samples from the GLCL PA were as high as 29.9 mg/L. Concentrations of Ra were generally higher in waters from the limestone aquifer systems than in the glacial aquifers (Table 3) indicating that perhaps a greater proportion of the total adsorption sites are unavailable (removed, or not formed initially, or saturated) for the limestone aquifers with ongoing Fe and Mn reduction and dissolution than for the glacial aquifers.

Interplay of a variety of geochemical mechanisms may affect the Ra concentrations as water composition evolves and TDS increases. Bicarbonate was most commonly the predominant anion among the sampled waters, but among those that were more mineralized, high concentrations of SO_4 and Ca were present as well, and the SO_4-dominated water type was commonly encountered (sampled). Many samples of SO_4-dominated waters did not have detectable concentrations of Ra isotopes. The SO_4-dominated water type, however, also had combined-Ra concentrations greater than the MCL with high frequency of occurrence – 12.76% (12 of 94 samples) – significantly higher than from HCO_3-dominated water types (Table 3). The overall concentration trend for the SO_4-dominated water type showed that ^{226}Ra, Ba and SO_4 concentrations were inversely correlated (Online Supplemental Table S-7).

The geochemistry and geology of the Ra-poor and Ra-rich samples from the SO_4-dominated waters are examined in turn. The waters containing the elevated concentrations of Ra and dominated by SO_4 were primarily anoxic as indicated by the low concentrations of DO and by high concentrations of Fe (Fig. 10). Concentrations of Ra isotopes, especially those of ^{226}Ra, correlated strongly with concentrations of Fe in SO_4-dominated and in HCO_3-dominated waters (r, +0.521 and +0.397, respectively; Online Supplemental Table S-7). On the other hand, the Ra-poor and SO_4-rich waters were oxidizing as was indicated by the high DO and low Fe concentrations (Fig. 10). Of the 38 samples of near-neutral to alkaline SO_4-dominated waters with concentration of DO > 1.1 mg/L, none contained combined Ra in excess of the MCL and the concentrations rarely exceeded 0.037 Bq/L. The inverse trend among Ba and SO_4 concentrations (Fig. 11) implies the possibility that barite precipitate may form, or at least that excess SO_4 minimizes Ba solubility. Calculation of the saturation states of the SO_4-dominated water samples with respect to barite indicated that they were uniformly at saturation with respect to barite (97.8% had positive saturation index (SI), Fig. 11). About half (48.2%) of the HCO_3-dominated waters were at saturation with respect to barite.

The generally alkaline and oxic SO_4-dominated water type samples (high SC and high SO_4 with concentrations that in some samples exceeded 1000 mg/L, but low in Ra) were mostly from the arid western USA, from the MWAF, PCAF and RGBR PAs (Table 1). Evapotranspiration is likely to increase the TDS considerably there. The formation of barite precipitate is possible if a steady source of Ba to solution is available, which the considerable weathering of the immature alluvial and basin-fill sediments is likely to supply (Reynolds et al., 2003), in the oxic environment, the formation of Fe- and Mn-oxyhydroxides results from the weathering of Fe- and Mn-bearing minerals. Many of the alluvial-fan and fluvial unconsolidated sand deposits of the PAs in the western USA do not contain electron donors (organic C) at sufficiently high concentrations to consume available DO and establish an anoxic environment (McMahon et al., 2004; McMahon and Chapelle, 2008). For 25 SO_4-dominated samples that were saturated with respect to barite and Ra radionuclide concentrations were <the SSMDC, the concentration of Fe was most typically about 10 lg/L or less and exceeded 100 lg/L in only 7 (28%) (Fig. 10). Adsorption of Ra is likely, foremost rapidly onto abundant Fe- and Mn-oxyhydroxides (Krishnaswami et al., 1982). The possible rapid co-precipitation of Ra with barite may operate in conjunction with the sorptive processes to limit the Ra concentrations. Barite formation as a sink for Ra has been documented at mine-waste sites in the western USA (Martin and Akber, 1999).

Samples with high concentrations of SO_4 and of Ra that commonly exceeded the MCL were anoxic in character and were most often from the MCOO PA, and occasionally from the FLRD PA. The materials comprising these PAs contain electron donors (organic C, sulfide minerals) and beds with low permeability matrix that form effective confining units, and anoxic geochemical settings are common (McMahon and Chapelle, 2008). For the 12 SO_4-dominated samples that were saturated with respect to barite and yet had concentrations of combined Ra that were P the MCL, the concentrations of DO were 6 1.1 mg/L and the concentration of Fe exceeded 100 lg/L in 10 (83.3%) (Fig. 10). In many of the SO_4-dominated waters, little Ba is present in solution (typically less than 10^{ffi7} moles/L; Fig. 11). With little Ba present, it is possible that barite micro-crystals do not nucleate readily to allow formation of even minor amounts of barite precipitate, or the barite precipitation rates may be very slow. The Ra supply to the ground water, in contrast to Ba, is not only a function of weathering, but also is

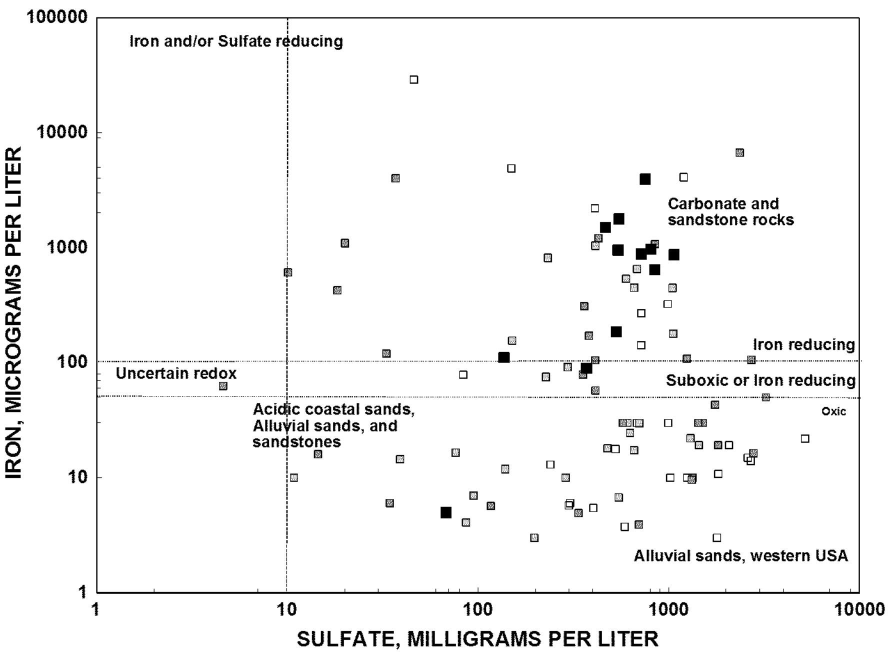

Fig. 10. Relationships between concentrations of SO_4 and Fe in water samples in which the SO_4 anion is predominant from 15 principal aquifer systems of the USA, 1993–2005, with the range of concentrations of combined Ra (^{226}Ra plus ^{228}Ra) indicated. [Concentrations of combined Ra: open, small symbol, less than (<) sample-specific minimum detectable concentration; light gray, small symbol, quantifiable concentration < 0.037 Bq/L; dark gray, small symbol, greater than or equal to 0.037 Bq/L but < 0.185 Bq/L; large, solid black symbol, P 0.185 Bq/L. 1 Bq/L = 27.027 pCi/L.]

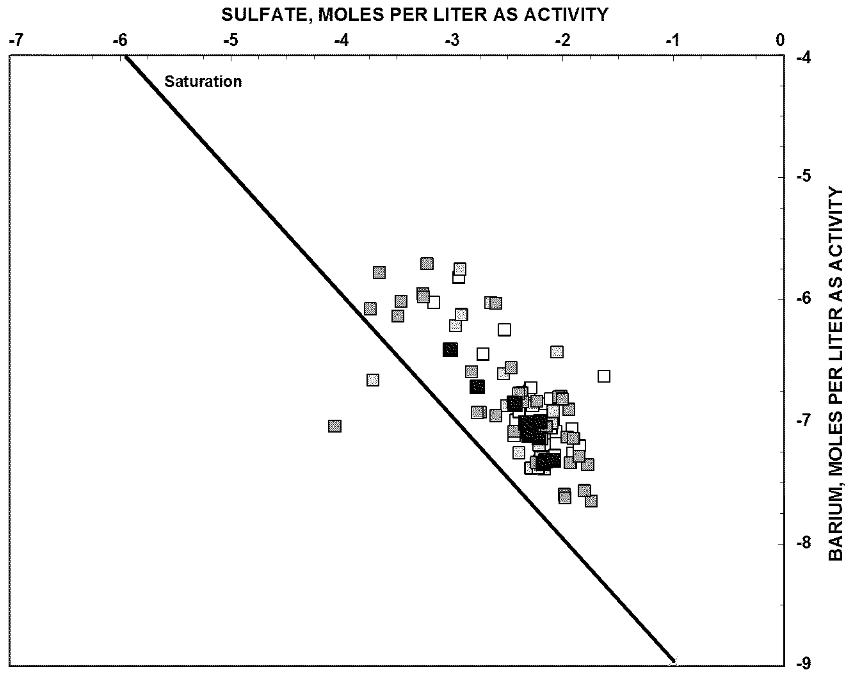

Fig. 11. Relationships between concentrations of SO_4 and Ba in samples in which the SO_4 anion is predominant from 15 principal aquifer systems of the USA, 1993–2005, with the range of concentrations of combined Ra (^{226}Ra plus ^{228}Ra) indicated. [Diagonal line is the line of saturation for water with respect to barite using a value for barite solubility product at saturation of $10^{ffi9.97}$. Concentrations of combined Ra: open, small symbol, less than (<) sample-specific minimum detectable concentration; light gray, small symbol, quantifiable concentration < 0.037 Bq/L; dark gray, small symbol, greater than or equal to 0.037 Bq/L but < 0.185 Bq/L; large, solid black symbol, P 0.185 Bq/L. 1 Bq/L = 27.027 pCi/L.]

a function of alpha recoil from mineral grains or surfaces (Fleischer, 1980; Reynolds et al., 2003). The relative amount of Ra in comparison to the Ba may increase as Ra is released from both weathering and recoil processes, and in the absence of sinks that may rapidly uptake Ra, the Ra released by alpha recoil may become a critical Ra source. The Ra/Ba molar ratio in the water will increase with residence time. The increase in concentrations of Ra and in the molar Ra/Ba ratio is notable in carbonate-rock type aquifers because sorptive oxides and clays are often low in the aquifer matrix to begin with, and in the anoxic environments, the relative Ra adsorption coefficient is likely to remain low (Krishnaswami et al., 1982). Slow barite precipitation in these circumstances is likely an inefficient sink for Ra. Grundl and Cape (2006) advanced a similar hypothesis for samples they analyzed from along groundwater flowpaths from the MCOO PA.

Additional geochemical mechanisms may contribute to providing the conditions for occurrence of elevated Ra concentrations in SO_4-rich anoxic waters. A decrease in Ra partitioning into any barite that does form may be likely, especially in Ca-rich waters where barite precipitation itself is limited in amount and is kinetically slow (Sturchio et al., 2001; Eikenberg et al., 2001; Arndt, 2010). The presence of elevated Sr concentrations may limit Ra uptake in barite (Ceccarello et al., 2004), and so may increasing temperatures (Langmuir and Melchoir, 1985), a factor for anoxic waters at depth. Concentrations of Ca ranged from 80 to 280 mg/L and those of Sr ranged from 1200 to 7440 l g/L in these samples. Celestite, the sulfate salt of Sr, is capable of taking up Ra, but is slightly more soluble than barite. Concentrations of Sr correlated strongly and significantly positively with concentrations of ^{226}Ra and combined Ra in all water types, including where SO4 is the predominant anion (r, +0.256; Online Supplemental Table S-7), and in 9 of 15 PAs including the MCOO (Online Supplemental Table S-5). Therefore, it is unlikely that co-precipitation of Ra with celestite is a control on limiting Ra concentrations in these ground waters used for drinking. Sulfate-reducing conditions in some producing zones at depth in the thick MCOO PA (Gilkeson and Cowart, 1987) may limit barite precipitation or may enhance barite dissolution and thereby insure Ba and Ra solubility at particular depth intervals. Waters from zones high in SO_4 may mix with waters from zones high in Ra and low in SO_4, and may thereby affect the Ra content of the collected water sample. Indicators of mixed redox conditions (McMahon and Chapelle, 2008) were common from the GLCL and MWFT PAs, and (parts of) the CPTG, MCOO and MWAF PAs, implying mixing along sharp concentration gradients.

5. Implications of understanding geochemistry of radium occurrence

Results from this study detail how Ra occurrence can vary in wells from different geologic regions or PAs in the USA on the basis of different geochemical environments. The broad generalized assessment can be made that aquifer materials with low sorptive capacity such as limestones or mature (quartzose) sands in combination with geochemical properties that minimize adsorption efficiency including acidic, anoxic/suboxic, and mineralized conditions correspond to provide the highest likelihood of Ra occurrence (Tables 3 and 5). Most commonly, when the underlying bedrock/sediment is characterized by high organic-C content or high degrees of confinement with little influx of DO-rich water, contact between the water and the sediment material leads to consumption of electrons, onset of anoxic conditions, and reductive dissolution of Fe and Mn that limits potential Ra sorption to reactive oxyhydroxides of these metals, with ensuing relative increase in Ra mobility. The lesser relative amounts of adsorption of Ra likely leads to the increase in Ra concentration even where Ra, U and Th are not abundant in the aquifer matrix and concentrations of U and ^{222}Rn in the waters are low (Table 3).

A limitation of this study is the degree of uncertainty at the local scale given aquifer-wide variability of physical and geochemical factors that may mobilize Ra. Geochemical variability may be large locally as a result of depth differences, for example. The sampled well types and well depths were not distributed evenly among the PAs (Table 1) precluding detailed assessment of effects of such local variability. The Ra occurrence nationwide is broadly controlled by geochemical properties (the frequent presence of elevated concentrations of Ra in reducing waters), but is not directly, simply, or uniquely defined by the occurrence pattern of any single surrogate constituent (such as high Fe; see Online Supplemental Table S-5) but depends on multiple geochemical factors. A single nationwide Ra occurrence model does not fit because of the multiple geochemical environments for Ra occurrence (mobilization). Factors related to geology and climate affect, to some degree, the acidity, redox potential, degree of mineralization, and composition of ground waters, as well as their potential residence time, and each of these factors can exert local control on sorption properties and thereby also affect the occurrence pattern of the isotopes of Ra.

The information broadly detailing Ra occurrence and typically associated geochemical environments can be particularly useful to private homeowners with domestic wells, because these water systems generally are not monitored regularly for Ra (DeSimone, 2009), unlike public-supply wells that are monitored under the Safe Drinking Water Act (USEPA, 2000a; Focazio et al., 2001). More than 40 million people in the USA consume water from these private wells that are not regulated or monitored and could pose a source of exposure. The Ra-occurrence data and associated geochemical data collected from large-scale regional studies such as this one (and perhaps data that is measured locally in the public-supply wells), could be applied with an understanding of the broad geochemical conditions (anoxic/suboxic, acidic, mineralized) in which Ra may be elevated to provide assistance to private-well owners in identifying where the risks are highest and can guide the prioritization for testing (actual data collection) from private wells in these areas. The random measurement of only the gross alpha-particle activity of the water samples without knowledge of the broader context of the geochemical environments may not provide enough information to assess Ra occurrence and exposure to it because the amount of alpha radioactivity emission is controlled more often by the occurrence of U than of Ra (Table 4). Concentrations of Ba, Sr, Fe and Mn consistently correlated with concentrations of all the Ra isotopes in nearly all the PAs (typically in 9 of the 15) and geochemical conditions (Table 5; Online Supplemental Table S-5), and among the samples, concentrations of Ra correlated directly, whereas concentrations of U correlated inversely, with concentrations of Fe (Table 5; Online Supplemental Tables S-6 and S-7). Thus, the concentrations of these constituents are of interest because, especially when coupled with measurement of the gross alpha-particle activity in particular geochemical environments, they might provide an indication of the general potential that elevated levels of Ra are present when the actual Ra concentrations have not been determined.

The usefulness of the implementation of these findings is illustrated in the testing of domestic wells in the CPNA PA in New Jersey. Guidelines for New Jersey's Private Well Testing Act (New Jersey Register, 2002) require testing and analysis for gross alpha-particle activity in water from domestic wells because a local study demonstrated the frequently occurring presence of elevated concentrations of Ra were associated with elevated gross alpha-particle radioactivity in the strongly acidic waters (Szabo et al., 2005), whereas U concentrations were low in that environment. The knowledge gained of the geochemical environment allowed the well-water testing program to be optimized within the specific aquifer system by focusing on the quick and inexpensive gross alpha-particle activity analysis. The findings from the larger-scale study reported here confirm the inverse correlation of concentrations of combined Ra with pH for the CPNA PA (Fig. 9 and Table 5; Online Supplemental Tables S-5 and S-6) and imply that the optimized testing program could be applied on the regional scale for the aquifer system. The Ra, when occurrence is identified, can readily be remediated (lowered or removed) by homeowners with a well-maintained water softener (cation exchange) system (Lucas, 1987; Szabo et al., 2010). Continued public education and testing of domestic wells is advisable (DeSimone, 2009; Treyens, 2009), particularly in those PAs and in those geochemical conditions in which relatively high drinking-water occurrence frequencies for Ra were identified in this study.

6. Conclusions

Broad trends in Ra occurrence within the USA are delineated in the context of the geological and geochemical framework provided in this assessment that is the first to not only characterize the occurrence of the three major isotopes of Ra throughout much of the USA using data collected in a consistent manner, but also to assess their occurrence with respect to geochemical environment. Seven principal aquifer systems (PAs) of the 15 studied were identified in which the exceedences of the US Environmental Protection Agency maximum contaminant level of 0.185 Bq/L (5 pCi/L) for combined Ra (^{226}Ra plus ^{228}Ra) occurred in 39 (4.02%) of 971 samples for which both ^{226}Ra and ^{228}Ra were determined, and in 40 (3.15%) of 1266 samples in which at least one of these isotopes were determined. The Ra occurrence is broadly controlled by the geochemical properties of Ra, primarily sorption, desorption, and exchange, and possibly co-precipitation with barite in the most SO_4-rich and oxic regions. When the underlying bedrock or sediment comprising an aquifer system has characteristics (high organic C, hydrologic confinement) that leads to rapid consumption of oxic species, or is composed of materials that have poor acid-neutralizing or sorptive capacity (extremely quartzose sands or carbonate rocks), relative increase in Ra mobility (lesser amount of adsorption) is likely even if Ra is not abundant in the bedrock or sediment. Concentrations of combined Ra greater than the MCL were most commonplace in the MCOO and the CPNA PAs because of favorable geochemical conditions (anoxic mineralized or acidic waters, respectively) that enhanced Ra mobility. The presence of anoxic geochemical conditions were related to the occurrence of Ra concentrations that exceeded the MCL in one or more samples in the APMB, CNEY, FLRD, CPTG, and GLCL PAs, and were related to occurrence of lesser but detectable concentrations in the MWFT, APVR and HPTA PAs, as was a combination of acidic and anoxic conditions in the CPSE PA. In each PA with these broad geochemical conditions, other indicators of radioactivity and geochemical environment such as gross alpha-particle activity in association with concentrations of Fe, Mn, Ba and Sr are of interest because they provide indirect information of the possible presence of elevated concentrations of Ra, though specific occurrence patterns vary locally.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apgeochem.2011.11.002.

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